QUANTITATIVE STUDIES IN PHOTOCHEMISTRY OF DYES

by

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PUBLICATIONS

The work described in this thesis has been included in the following papers.

Part III. Statistical Relation between Molecular Geometry of dyes and their Light-Fastness. By Hojiwala et al. Text. Res. Jour., 36, 587 (1966).

In preparation:

Part I. Influence of high temperature on fading of synthetic fibres.

Part II. Quantum efficiency of fading of dyes in fibres.

SUMMARY

The first part of this thesis deals with the effect of temperature and humidity on the fading of dyes on polyamide (nylon) and polyester film substrates and also on gelatin and regenerated cellulose film (Cellophane). The results of fading obtained with disperse dyes on polyamide and polyester substrates were found in all cases to give first-order plots. This shows that dye in the substrate is probably either monodisperse or present in very small aggregates.

The influence of temperature on fading of dyes on nylon and on polyester was quite considerable. In fact it was opposite to the general trend on hydrophilic substrates which is that the rate of fading decreases with increase in temperature, because of loss of moisture by the fibre. The present effect with substrates which normally contain very little adsorbed moisture, might be due to change in the internal structure of the polymers when heated to a high temperature or simply to the normal effect of temperature becoming operative when the adsorbed moisture is almost entirely removed.

The rate of fading test results obtained with cellulose and gelatin show that the dye in these two substrates

is probably present partly monodisperse and partly as aggregates. Increase in humidity greatly increases the rate of fading.

Experiments to determine the quantum efficiency of dye fading on the substrate are described in the second part of this thesis. Disperse and direct dyes were applied to nylon and Cellophane films respectively. The dyed films were faded under different filters and the quantum efficiency values calculated. The values thus obtained were much lower than those which are recorded for fading of dyes in solution. This probably shows that most of the radiant energy absorbed is dissipated as heat, though in some cases it might partly have been used up in causing tendering of the substrate.

The third part of the thesis describes some calculations made to reveal if any relation exists between the molecular geometry of dyes and their light-fastness. Selected dyes from various groups for which Colour Index data are available were examined. The results were plotted as molecular axial ratio (MAR) i.e. ratio of molecular length to width, against the light-fastness grade. Only in the case of anthraquinone vat dyes on cotton was any significant relation found.

This was an inverse one, i.e., light-fastness decreases with increase in MAR. Direct, disperse and acid dyes did not show any significant relation.

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GENERAL INTRODUCTION

Among the properties desired in dyed materials, fastness to light is of great importance and the standardisation of technique for the assessment of fastness to light has therefore received considerable attention. The action of light on dyed fibres depends on the nature of the dye and of the fibre, on the other constituents of the dyed fibre, on the composition of the atmosphere, and also of course on the nature of the source of light. The colour of a dyed material is the direct result of its visible absorption spectrum, which is of course determined by the molecular structure of the dye, and influenced by the degree of aggregation of the dye present.

State of dye in the fibre

Fading seems to depend to a considerable extent upon the state in which the dye exists in the fibre. Three general methods have so far been used to determine the state of dye in the fibre. These are now described.

(a) The absorption spectrum of most dyes in the visible region shows two bands, the short wave (y) band representing associated dye and the long wave (x) band, representing mono disperse dye. It has been shown[1-2] that increase in the ratio of y/x, extinctions usually

indicates an increase in degree of association, though recently Hillson and McKay[3] have doubted whether this is a universal rule.

(b) The slope of the CF (characteristic fading) curve (i.e. log of time t_f for a given loss of dye, vs. log of initial concentration) can also give some qualitative information on the state of association of dye in the substrate. It has been shown[4] that in place of log t_f the fastness grade number may be plotted and similar curves can be obtained which are called "characteristic fastness grade" - CFG curves. These also give some information on the physical state of the dye in the fibre.

Water-soluble dye molecules are large and have strong intermolecular attraction of various kinds. When the dye molecules make a contact with a surface of fibre and lose their protective shell of water, these intermolecular forces then come into action resulting in a formation of associated particles.

It is well known that water-insoluble dyes (e.g. azoic and vat dyes) form amorphous particles or actual crystals in the fibre, as shown by Sumner[5] et al but upon the nature of the "micelles" of water-soluble

dyes very little information is available. It is believed that the micelles of low light fastness direct dyes in cellulose, of many acid dyes in proteins and perhaps those of disperse dyes in hydrophobic substrates are very small and may contain only a few dye molecules.

It appears very difficult to obtain absorbed dye in truly mono-disperse form in a solid substrate. A truly mono-disperse dye should fade at a rate that decreases exponentially with time, i.e. a first-order reaction rate (as indeed should relatively small dye aggregates).

Fading rate curves of water-soluble dyes show an initial rapid fade, of nearly first-order; but this persists for only a short period, and the rate then quickly slows down, and may sometimes become almost zero-order. The most reasonable interpretation of this type of curve seems to be that a small proportion of the dye is highly dispersed but most of it is aggregated. It seems therefore reasonable to assume that a linear fade is evidence of a high degree of aggregation.

It has been shown[6] that dye light-fading reactions

in the atmosphere are influenced by the extent and the nature of the air-dye interface. It is believed that the smaller the surface area exposed, the less rapid should be the fading. Early evidence in support of the above statement comes from Bean and Rowe[7] who found that the microscopic crystal growth of insoluble azoic dyes on cellulose fibres, caused by after treatment such as soap boiling or steaming, reduced the surface area of the dye and hence improved the light-fastness. According to Rahman[8] any form of aggregation which decreases the surface area of the dye will improve the light-fastness but its exact effect will depend upon the nature of the aggregation.

The influence of dye concentration on light fading

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By the normal laws of photo-chemical change light-fastness should increase with the dye concentration above the concentration at which all the incident active light is absorbed even if the dye is entirely in molecular disperse form. Beyond this point no more dye can be decomposed, so that as the dye concentration rises the proportion of total dye faded decreases and hence the apparent light-fastness increases.

Barker, Hirst and Lambert[9], while fading wool

cloth dyed to different percentage depths of shade with different dyes found that when the amount of dye remaining after the exposure was plotted against the amount originally present, a straight line was obtained of slope approx. 1.0, but not passing through the origin. (The line of no fading would be a line of slope 1.0 passing through the origin). The explanation given for this was that a given amount of energy can cause the same destruction of the dye, whatever the amount originally present. This is the condition normally obtaining in photo-chemical reactions when the whole of the active radiation is absorbed, the number of molecules decomposed then becoming proportional to the time of exposure. This is known as a reaction mechanism of zero-order.

Eaton, Giles and Gordon[10] have found that a linear relation exists between light-fastness grade number and the logarithm of dye concentration on the fibre.

Baxter et al.[11] first described the method of plotting the logarithm of time (t_f) required for a given percentage loss of dye by fading (usually a 10% loss is chosen) against the logarithm of the initial

dye concentration (Co). The t'_f values in these linear curves so obtained were later shown by Giles[4] to be equivalent to a fastness grade on the normal geometrical scale. Usually with water-soluble dyes the OF and CFO curves have a positive slope, due either to an increase in proportion of larger particles with rise in concentration, or to decreased accessibility of their surfaces to moisture and air, etc.

In the case of a very few disperse dyes on hydrophobic fibres it was found[4] that an increase in dye concentration decreased the light-fastness. This effect is of course opposite to the general trend of most observations which is that an increase in dye concentration increases the light-fastness. This anomaly is believed to be due to one or more of the following causes:

(a) with rise in dye concentration a large proportion of dye remains mono-disperse having penetrated into more crystalline parts of the substrate, where the restriction of the surrounding polymer chains prevents it from associating;

(b) the presence of large dye micelles in regions of the substrate inaccessible to water, tends to distort

the fibre polymer molecules making it easier for air and water vapour to penetrate the substrate near the dye micelles. If this distortion is more pronounced at higher dye concentration then the accessibility will increase with concentration and the fastness will fall; (c) the particular (and so far unknown) mode of association of dye molecules in the aggregates facilitates photolytic breakdown.

The influence of chemical structure of dyes upon light fading

The recorded tests have usually been made on cellulose and the results have shown that substituents which increase the resistance to oxidation also increase light-fastness. Parallel tests on protein substrates[6] usually show an opposite effect; increased resistance to oxidation gives decreased light-fastness.

The influence of ortho-substituents

According to Atherton and Peters[12] hydroxy-groups substituted in the ortho-position to the azo-group appear to improve light-fastness on both protein or nonprotein substrates. They attributed this to the protection afforded to the azo-group by the chelate

ring in which it thus became involved. They also noticed that a methoxy group improves light-fastness in the ortho-position but lowers it when meta or para, and attributed the ortho-position effect to steric protection of the azo-group.

The influence of meta and para substitution

Kienle et al.[13] and Finke and Miller[14] have established the influence upon fading of substituents meta and para to the azo-group in benzene azonaphthalene dyes. The effect of meta and para substituents will depend on whether or not they exert a protective effect on the azo-group, which must be the point of attack in fading. Thus Cumming et al.[6] have shown that the electronegative groups, e.g. $-NO_2$, decrease the fading rate on non-proteins and increase it on protein fibres. Electropositive groups such as $-OCH_3$ behave in the opposite sense.

It has been found that in general the logarithm of relative rate of fading of a series of meta and para - substituted azo dyes form a linear plot with the σ values as determined by Hammett[15]. The sign of the gradient of the line obtained varies according to the substrate in which the dye is contained.

Evidence of oxidation in light-fading

There are more evidences of oxidation than reduction taking place during light fading. Harrison[16] had observed that in sunlight or low intensity ultra violet light the fading of Methylene Blue on cotton appeared to be an oxidative reaction and when several dyes were exposed in evacuated or nitrogen-filled glass tubes, they did not fade at all.

Haller and Ziersch[17] obtained oxidation products from the fading of insoluble monoazo dyes on cotton. Couper[18] by a chromatographic method, identified a variety of oxidation products from the fading of 1:4, bis(methylamino)anthraquinone on cellulose acetate.

An attempt was made by Desai and Giles[19] to show that the increased light-fastness imparted to azo dyes on cellulose by nitro- and chloro- substituent groups, is due to the effect they have in increasing the resistance of the dyes to oxidation. They also observed adverse effects on light-fastness from the presence of electropositive groups such as methoxy and methyl groups.

Influence of temperature and humidity on the light fading

It is well known that the rate of fading of some coloured materials varies considerably with moisture

available. When pieces of tannin-mordanted cotton dyed with the basic dye Acronol Yellow 2G (C.I.815) were placed in two sealed bottles, one containing water and the other anhydrous calcium chloride, and both were exposed to light side by side, the pattern exposed in the damp atmosphere was completely bleached long before there was any detectable fading on the one kept dry[40].

Hedges[20] was probably the first author to examine quantitatively the part played by humidity and temperature in light fading. He found that with either wool, silk or cotton, reduction in moisture content decreased the fading rate. In this connection he used aqueous solutions of glycerol or certain salts to obtain the different humidity values. These solutions were placed in small boxes containing horizontally fixed dyed patterns behind a Vita-glass window for exposure to a "Hanovia" quartz mercury vapour lamp. The moisture content and the effect of temperature change at various humidities were observed and the temperature coefficients were calculated at various temperatures over the range 10-50°C. The values obtained were quite in agreement with observation made earlier by Schwerzaw[21]. Fading was found to be accelerated by a rise in humidity in

all cases; a linear relation appeared to hold between percentage loss of dye and the moisture content of the sample, at least down to ca 5% moisture content for a number of dyes on cotton or wool, but in the case of silk it was found that at 10% moisture content the curve of colour loss against moisture content becomes much more steep.

The Equation,

$F = K\ T\ (R+C)$, where

F = % loss of dye, K and C are constants, T is the temperature and R is the regain of the fabric, suggested by Hedges[20], enables one to predict the percentage loss of dye after fading under different conditions, but observations made by Lead[22] showed that moisture content of exposed fabrics could not directly be determined from the humidity of the surrounding atmosphere since the exposed sample may be at a higher temperature than the atmosphere. This has been confirmed by Nordhammar[23], who found that the temperature of the samples in the Fade-Ometer fading lamp fluctuated round a temperature as high as 90°C, with a fabric humidity much lower than to be expected from the condition of the atmosphere inside the lamp.

It has been shown by Hedges[24] that for many dyes the increase in rate of fading is proportional to the amount of absorbed moisture. If the percentage fading is plotted against absorbed moisture a straight line is obtained, the slope of which is a measure of a susceptibility of the dye to humidity. Cunliffe[25] also made out similar investigations in fading a number of dyes on wool at two different temperatures and humidities. The eight light-fastness standards were in fact chosen for their relatively low sensitivity to moisture during fading, but the results Cunliffe obtained indicated that the fading of some of the standards were considerably accelerated by the moisture.

A study of the effect of artificial fading lamps on fading must include the effect of humidity and temperature. As already described these effects are normally interdependent since an increase in temperature proportionately decreases the atmospheric humidity. It has been found that fading rate increases with increase in temperature providing that the moisture content remains the constant. The magnitude of increase occuring over the range of temperature encountered in light-fastness testing is probably much

smaller than that resulting from humidity variations. This view was also held by Hoffmann[26] and by Lead[22]. The greatest variation recorded in the literature is that at 100% relative humidity Solway Blue R on wool faded 4.5 times as fast at 140°F. as at 77°C., at lower humidities the effect is much less, and the ratio at 32% R.H. is only 1.7. Many American workers however, believe the converse to be true, for example, Norton[27] has stated that there were indications that the specimen temperature was perhaps the greatest single contributing factor influencing the rate of fading. The temperature of the specimen depends on two factors. Firstly, the pattern will start by having the same temperature as the surrounding air (providing this is stable enough for equilibrium to be reached). Secondly, the specimen exposed to a light source will absorb radiant energy, and all that which is not used photochemically will be converted to heat and will thus raise the temperature of the specimen above that of the surrounding air.

As testile materials are generally poor conductors of heat, there will often be a pronounced temperature gradient between the exposed face of the specimen and

the back, but it is only the surface temperature which is important in fading.

As stated earlier, moisture accelerates fading while dry conditions (as at high temperatures) retard fading. This applies to hydrophilic fibres. The effect on dyed hydrophobic fibres is sometimes different, in that the temperature rise may cause marked acceleration in fading. The most recent work to investigate the effect of temperature and humidity was carried out by Morris[28]. The main purpose of his work was to determine what effect heat or humidity may have upon the light-fastness of dyestuffs applied to different hydrophobic fibres. A large number of samples of synthetic fibres, e.g., Dacron, nylon, Dynel, Orlon, etc., were exposed in a special research model Fade-Ometer and in daylight. The main advantage of this specially made Fade-Ometer was that it was possible to control the humidity and temperature quite accurately. Three different temperatures, viz, 135, 155, and 175°F; and three relative humidities, viz, 35, 50, and 65% were used. The daylight exposures were made in a weatherproof cabinet.

Examinations of the exposures in the above mentioned conditions showed that in general, increase in temperature had much more effect on both fibre and dyestuff than did increase in relative humidity. Similar observations were made[29] by exposing seventy-five samples of synthetic fibre to the temperature 185°F in a special Fade-Ometer, and it was found that rate of fading was considerably faster at this temperature.

The evidence appears to suggest that it is a severe loss of moisture in these dyed hydrophobic fibres, which causes greatly accelerated fading and that this loss occurs only in special circumstances. This effect is of course opposite to the general trend of most observations in dye fastness testing, which is that dryness retards fading.

It was at first thought, that some new factors appearing under anhydrous conditions must be responsible for this anomalously rapid fading, and one object of the present work was to determine whether this supposition is correct.

The influence of the chemical nature of substrate on fading

Cumming et al.[30] examined the rate of oxidation and of reduction in aqueous solution, and of fading in films of a protein (gelatin) and of a non-protein (methylethyl cellulose) of several dyes of different chemical nature. They concluded that oxidation occurs more readily on non-proteins and reduction on proteins. It was also shown[4] that when the fibres are of a different class the dyes of low light-fastness tend to have better fastness on proteins than on non-proteins and the dyes of high fastness tend to have better fastness on non-proteins.

Fibres of low regain

According to Giles[4] the general rule followed by many dyes is that light-fastness improves with rise in fibre regain. But in the case of many synthetic fibres the reverse is true. Thus many disperse dyes have higher light-fastness on polyester fibre or on polyacrylonitrile fibre than on cellulose acetate. This observation was confirmed by examining statistically a very large number of published commercial light-fastness assessments. The results of further investigations in

this laboratory support the hypothesis that the anomalously high fastness of dyes on polyesters is probably due to the absence of sufficient moisture in the substrate to sustain the fading reaction under the test conditions.

Fibres of high regain

Giles[4] further pointed out that in the case of most hydrophilic substrates the light-fastness of any given dye when compared on two non-proteins or on two proteins is higher on that with the higher standard regain. This is attributed to the presence of larger dye micelles in the fibres with higher standard regain than in the others.

Anodic oxide films

Speiser[31] found that a few dyes, of the acid, metal-complex, and mordant classes have very high light-fastness on the anodic oxide film on aluminium, such that they withstand outdoor weathering for many years. Investigations here by Datye[30] have indicated that the cause is the process known as "Sealing", always given to the dyed films, whereby the pores of the oxide are blocked by development of hydroxide, the

treatment is given in boiling water or steam, just after dyeing. Giles and Datye[32] studied various factors influencing the light-fastness of anionic dyes on anodic oxide films on aluminium. The high light-fastness just mentioned appeared to be due to the blocking-off of a proportion (not all) of the adsorbed dye, by the sealing process, which prevents access to it of atmospheric oxygen and water vapour and so retards fading.

Absorption and dissipation of light energy

It is generally accepted that photochemical reactions are initiated by the absorption of light energy in the high intensity regions of the spectrum of the absorbing substance corresponding to the "permitted" transitions between singlet levels. When radiation falls upon the absorbing molecule, some of that absorbed, increases vibrational and rotational energy of the molecule or excites the electron system to a higher energy level. The latter situation is of great significance in photochemistry since an activated molecule is thus produced. Bowen[33] has described how the excited singlet level, when it passes on to a triplet level, is chemically more reactive and

has a longer mean life time than the excited singlet level. He further describes how the very low quantum yield of a photo-reaction of dye fading (10^{-6}) may quite possibly be due to the low probability of such transition taking place rather than to the very short life of the excited singlet level. The electronic energy of the excited dye molecule, after an interval of ca. 10^{-8} seconds can be degraded into heat energy by intermolecular collision, or be retransmitted as resonance or fluorescent radiation or it may initiate chemical and dissociation processes. A number of formal schemes to explain these latter "electron transfer" reactions have been presented by Bowen[33].

The mechanism of fading

As stated above the irradiated dye is excited perhaps to the triplet state and it then takes part in chemical oxidation or reduction reactions. Until the investigation of Hillson and Rideal[34] upon the photodecomposition of certain azo and triphenylmethane dyes was reported, little information was available upon the nature of the actual chemical species responsible for the oxidation or reduction of any type of dye in fading, though hydrogen peroxide was

known to be produced in some circumstances when dyes are irradiated. A volatile oxidising agent, suggested to be a meta-stable form of oxygen formed by a transfer of energy from excited dye to oxygen of the air[35] and capable of oxidising leuco-malachite green is formed by irradiating Acriflavine (C.I. 46000) dispersed on dry silica dust in dry oxygen at low pressure, but this dye does not form hydrogen peroxide on irradiation. It was concluded from the work of Hillson and Rideal[34] that the photoexcited dye molecule or radical must react with water molecules in the bulk of the solution to give an oxidised form of dye as a free radical, and hydrogen atoms.

$$D \longrightarrow D^{*}; \quad D^{*} + HOH \longrightarrow DOH + H$$

The free radical is unstable and reacts with a further molecule of water. The reaction mechanism was suggested to be direct addition of hydrogen atoms. The formation of free radicals was detected by the polymerisation of methyl-methacrylate in the dye solution when illuminated and also to some extent even in the dark. Hillson and Rideal[34] and also Schwen and Schmidt[36] recognised the essential function of water in acting as both an oxidising

and reducing agent in photodegradation of dyes. There is a correlation between a fading rate of many dyes on cellulose and the degree of photolytic tendering of the fibre. The tendering agent appears to be hydrogen peroxide or activated oxygen[35].

Fading effects of light of different wavebands

On first principles one would expect fading to become progressively less with increase in wave-length. But in practice this is not entirely true and investigations have shown that the relation between wave-length and fading power is a complex one.

Taylor and Elliot[37] found in their work on photochemical reactions that for monochromatic light the amount of absorbing substance removed per unit amount of energy absorbed was independent of wave-length throughout a wide range of wave-lengths. But in fading tests monochromatic light is seldom used. As a matter of fact a very wide range of wave-lengths (3000 - 8000A) is normally used for fading of different dyes on different substrates. Kobsa and Maerov[38] when studying basic dye fading in sunlight on a modified polyester fibre found that the most effective spectral region lies between

ultra-violet region. Observations made by Luszczak and Zukriegel[43] while fading some of the German blue fastness standards in sunlight were quite in agreement with those of McLaren. They[43] found that (a) there is a relation between fastness grade and the wave-length (λ) of a characteristic absorption waveband of the dye in the ultra-violet region. The shorter is this wave-length, the higher is the fastness rating; (b) fading is caused mainly by an absorbed waveband with a fairly definite upper boundary at about twice the characteristic wave-length (λ). Beyond this boundary the absorbed light is almost inactive.

Photochemistry is concerned with chemical reactions resulting from exposure of a system to radiation, normally in the visible or ultra-violet spectral regions (2000 - 8000A). Photochemical change is governed by two fundamental laws, (i) the Grotthus-Draper Law which states that only radiations which are absorbed by the reacting system are effective in producing chemical change; (ii) the Stark Einstein Law, which states that each molecule taking part in a chemical reaction induced by the exposure to light absorbs one quantum of the light energy. Experiments have

shown however, that this law is not always obeyed. Results are expressed in terms of quantum efficiency or quantum yield (ϕ) thus -

$$\phi = \frac{\text{Number of molecules decomposed}}{\text{Number of quanta absorbed}}$$

and on this basis, quantum yield can be unity, less than unity or more than unity, as in the case respectively, of the dimerisation of anthracene, the formation of ozone and the reaction of hydrogen with chlorine.

Relation between photochemistry of dyes and their light fastness

It is not yet known for certain whether the singlet or the triplet state of the dye molecule takes part in normal fading reactions, but some interesting tests are reported with model compounds and dyes to identify the species responsible for photolytic tendering of cellulose catalysed by vat dyes[44-45]. This species appears in fact to be the singlet state of the dye, but it seems at least possible that normal fading of other dyes may proceed via the triplet state, which has a life longer by several orders of magnitude

than the singlet state, and hence a greater chance of reacting with other molecules[46-47].

In theory the breakdown of an irradiated dye molecule could be retarted, and thus its light-fastness be raised by encouraging radiationless transitions to the ground state, e.g. by quenching the triplet state, if this is indeed formed. Quenching can be accelerated by the presence of a substance with a lower triplet level[48] or by paramagnetic ions. Therefore such substances might be added to the dyed fabric to improve the fastness. Little information is available upon the influence of the state of association of a dye on its liability to photolytic breakdown but the dye molecules are believed to be more stable in the crystal form than if they are monodispersed. According to Eyring et al.[49], molecules inside the crystal cannot so readily decompose because of the physical restraints imposed upon them.

The reaction order in fading

Baxter et al.[10] suggested that the apparent reaction order in fading is a characteristic parameter of a dye-substrate system, completely independent of the

order determined by studying the rate of fading curve for a single concentration of dye on a substrate. The latter was called the real reaction order. When a dye fading occurs in a true molecular dispersion under uniform irradiation, it is said to follow an "ideal" reaction order. The three reaction orders thus defined have the same numerical value, i.e. unity, where the dye is spread as a true monolayer in a substrate and only a small proportion of the active incident radiation is absorbed. The real reaction order then remains constant throughout irradiation since no change in average particle size can take place.

Quantum efficiency of fading

The measurement of quantum efficiency of a photochemical process in a solid is difficult and except for some experiments on the photographic process[50] it does not seem to have been attempted previously. There are two chief difficulties; firstly to measure the light absorbed and secondly to expose all the solid uniformly.

The photosensitising action of "titanium White" is of considerable technical importance and the study of photochemical reactions[51] involving powders has

been made possible by using dyed titanium dioxide. Titanium White is known to be the cause of the fading of paints in which it is incorporated. It has been observed several times[52] that the "tint" paints containing titanium dioxide fade rapidly regardless of the way in which the oxide is introduced. Similar effects have been observed in distempers, in wallpapers loaded with titanium dioxide and in viscose fibres delustred with this compound. The work of Goodeve and Kitchener[51] indicates that it is possible to make accurate quantitative measurements of photo-reaction in the solid state and to determine the effect of concentration and wave-length.

There seems to be very little information about work on the quantum efficiency of fading of dye solutions and no information about quantum efficiency of fading of dyes in fibres, though it is believed to be of very low magnitude (10^{-5} - 10^{-7}) [53]. However, some workers have tried to calculate the quantum efficiency of fading of some dyes in solution. Morton[53] has reported that many dyes fade by the action of a comparatively narrowband of wave-lengths near the absorption maximum of the dye, visible rather than

ultra-violet light being the more efficient, though the light in question did not extend beyond 3650A. An exception was noted with direct dyes on cotton, after treated with "Fibrofix" where the fading depended primarily on the radiation (3400 - 3900A) absorbed by the fixing agent itself. Atherton[54] (discussion on the paper by Atherton and Seltzer) gives some data based on the relation between the quantal energies at the various wave-lengths of maximum light absorption in a series of seven similar monoazo dyes, which they used in their main investigation, and their initial destruction rates. These data are not very conclusive, but they may perhaps show that the photo-reaction is most rapid in the region 4400 - 4450A.

For the fading of certain colour-coupled dyes in gelatin, Collins found that the quantum efficiency was at a maximum in the near ultra-violet and fell almost to zero in the centre of the visible region. At this point the energy is ca. 50 Kcal. per quantum, which is sufficient to break an oxygen-oxygen bond, as suggested by Burgess[55], and might therefore be expected to affect the dye to some extent. Bamford and Dewar[56] measured the quantum yield of a photochemical process

of auto-oxidation of tetralin in the presence of the vat dye Cibanone yellow R at 4500A and 4000A, and found it to be 0.007 and 0.03 respectively. The quantum yield for tendering, with a series of vat dyes, was of the order of 10^{-5}.

Oster[57] has quoted very low values ($2.2 - 2.4 \times 10^{-4}$) for the quantum efficiency of photo-oxidation of Acriflavin (C.I. 46000) in aqueous solution by light of 4360A, and has also stated that the quantum efficiency of fading of Rose Bengal is also very low; and that these two dyes are more susceptible to photo-oxidation than most other dyes. They are protected by binding to a water-soluble high polymer, e.g. nucleic acid, phosphoric acid or polyvinylpyrrolidone. This is presumably a viscosity effect, i.e. the reaction rate is determined by the chance that an excited dye molecule will collide with an electron acceptor[58].

Molecular geometry of dyes and their fastness

Several attempts have been made in the past and in recent years to correlate the chemical constitution of dyes with their fastness properties, but the frequent introduction of new synthetic fibres with

different properties has created some difficulties in such attempts. Different fibres exhibit different dyeing properties for a given group of dyes and hence the fastness properties of a particular group of dyes may vary with different fibres. It was thought that an entirely new approach to the problem might be worthwhile, in which the geometrical shape of the dye molecules might be related to light-fastness by statistical methods.

Statistical methods of analysis have already been used successfully in this laboratory in light-fastness studies, in determining the significance of the relation between dye concentration and light-fastness[59]. It was Meyer[60] who suggested that the dyeing of cellulose was an adsorption process in which the dye molecules align themselves alongside the cellulose molecules. The further study of this suggestion by Hodgson[61], Schirm[62] and others, has led to the conclusion that in order that a dye may have affinity for cellulose, the molecule must be capable of taking up a linear and planar configuration, and should contain polar groups. In contrast to this observation, the effect of constitution in wool dyes

is difficult to detect. The acid dyes most widely used on wool are the sodium slats of aromatic sulphonic acids. The early acid dyes were all of a very simple monoazo type, but it was soon observed that polyazo compounds gave dyes of much higher wet fastness on wool[63]. This observed effect was attributed to the increase in molecular weight or rather decrease in solubility, for if the molecular weight is increased without alteration of the number of solubilising groups, the wet fastness is increased.

The solubility of the dye molecules increases with increase in number of solubilising groups, but the wet fastness of the dye at the same time decreases. This may probably be due to the fact that solubilising groups have more affinity for water than for the fibre. Tolin[64] et al, revealed that the rate of dyeing of wool and gelatin with acid dyes decreases with increase in the number of sulphonate groups in the dye molecule thereby revealing a relation between the rate of diffusion and affinity of the dye for the substrate. The greater the affinity, the slower is the rate of diffusion. This relation is however is in opposite sense to that shown by Gilbert's[65] calculations, which appeared to

show that the affinity decreases by about 1 kcal/mole for each sulphonate group added to the dye molecule. Some attempts have been made to relate diffusion coefficient of the dye with its molecular weight or molecular size. Odajima[66] found a linear relationship between the logarithm of the diffusion coefficient and the square root of the molecular weight of dye in three series of disperse dyes, two of them anthraquinone and one azo types, on secondary cellulose acetate, and one of acid dyes in a co-polymer of nylon 6 and nylon 66.

High fastness to washing of chrome mordant dyes on wool has been attributed to various causes by different workers. Baxter[10] et al. suggested that it was probably due to the presence of aggregates, while Giles[67] had suggested earlier that it could be due to wool-chromium dye bonding. Race[68] et al. suggested that their high fastness is due to increase in molecular size and not to any type of dye fibre bond.

Planar dye molecules sulphonated only at one end are surface-active and show lower light-fastness than the corresponding symmetrically sulphonated ones[69]. A small increase in surface-activity, produced by the

introduction of a short alkyl chain, which increases surface-activity markedly, seems to have an adverse effect.

The importance of the physical state of the dye in the substrate has been extensively investigated in this laboratory[10-70] and it has been emphasised as one of the most important factors governing light-fastness. Many dyes, whether soluble or insoluble in water, are probably present in the fibre as heterogeneous collections of particles ranging from a monomolecular dispersion to large aggregates. Dean and Rowe[6] showed many years ago that after treatments such as soap-boiling, boiling in water, or steaming, applied to cellulose dyed with azoic dyes caused crystal growth and also increased the resistance of the dye to fading. This and that of Weissbein and Coven[71], who worked with direct cotton dyes, is probably the most definite evidence connecting light-fastness with the physical state of dye in the fibre. The structure of the dye molecule must control the uniformity of size of the adsorbed particles and the structure of the fibre must control the distribution and growth of the particles. Azoic and sulphur dyes seem to form a wide range of particles sizes, while vat and some direct dyes of good light

fastness seem to form large particles of uniform size[10]. Morton[72], while investigating the state of some direct dye molecules in a highly crystalline cellulose fibre (ramie) found that at least some of the dye seemed to be oriented as single molecules parallel to the cellulose molecular chains.

During application of vat dyes to cellulose, aggregation of the dye molecules takes place, because of the mutual molecular attraction (non-polar van der Waals forces) between the dye molecules, and the origin of affinity forces in vat dyes for cellulose appears to lie in non-polar rather than polar forces[73-74-75-76]. In addition to the polar forces there must be present non-polar van der waals forces, which can operate when complex aromatic molecules are brought in close contact with the substrate These short-range forces are additive and extend over the entire surface of the molecule. The results of affinity measurements confirm that affinity increases with increase in molecular weight, i.e. molecular complexity. Peters and Sumner[75] observed that simple anthraquinone derivatives are not at all substantive to cellulose, whereas 1-arylamido-anthraquinone dyes are substantive.

Datye et al.[76] studied the effect of hypochlorite on cellulose dyed with direct and vat dyes, and found that dyes with an amino group in both the end components are less susceptible to oxidation than those with an amino group in a similar position in only one of the two end components. They also found that the o-hydroxyazo compounds are oxidised more easily than the corresponding o-aminoazo-dyes, and that unsubstituted benzidine dyes are less susceptible to oxidation than the corresponding o-substituted benzidine dyes. It is found that symmetry of substitution in disperse dyes reduces their solubility in water and their maximum adsorption by cellulose acetate, possibly because intermolecular forces are more powerful, and so can help to form more stable crystallites[77]. Increased stability of the crystal structure of symmetrically substituted anthraquinone dyes, produced in this way, may be the cause of their high light-fastness on polyester fibre (Terylene)[78].

Sekido[79] observed that the presence of free amino- or hydroxy-groups in the molecule of direct cotton dyes tends to reduce fastness.

EXPERIMENTAL

PART I - INFLUENCE OF TEMPERATURE AND HUMIDITY ON FADING

The source of irradiation.

Sunlight has usually been considered to be the best source of irradiation for the evaluation of light-fastness of dyed fabrics for commercial purposes. But some of the difficulties are quite obvious in using sunlight, e.g. variation in intensity and spectral energy distribution with the time and season of the year. Moreover the composition of the atmosphere in which the dyed fabrics are exposed to sunlight also varies from place to place and to a very great extent in between different countries. In addition to all these difficulties fading in sunlight is a very slow and tedious process. For these reasons different artificial light sources have been developed from time to time. Mostly these have been various forms of arclight.

There are three principal types of arc namely; the enclosed flame arc, the low intensity arc, and the high intensity arc. It has often been observed that fading results by artificial light and by daylight often differ to a great extent[80]. Gasser and Zukriegel[81-82] have described an apparatus named the "Heliotest" in which sunlight is collected by a lens system and concentrated on the patterns under test, whereby a

twenty-five fold increase in intensity is obtained. The limitation of this apparatus is that the output resembles sunlight only to the extent that the proportion of the radiation power emitted in the 3000 - 4300A° region is approximately the same as that of noon summer light, and moreover a good deal of heat is also said to be concentrated on the patterns.

A 400W high pressure mercury vapour General Electric "Osira" lamp with appropriate choke in series but without condenser was used throughout the present work. This lamp has the advantage of having a relatively constant emission over long periods, low running costs and of requiring very little attention. The lamp is held in a porcelain lamp holder screwed to a wooden baseboard and surrounded by a cylindrical sheet aluminium screen (17 ins. dia. x 15 ins. high) fitted at vapour-stream level with ¾ ins. wide aluminium shelves. As the source of illumination is a vertical incandescent vapour, the intensity of emission was considered to be relatively constant in any lateral direction hence the construction of a rotating pattern holding device was considered to be unnecessary. The air temperature within the screen was found to be constant (63°C) for

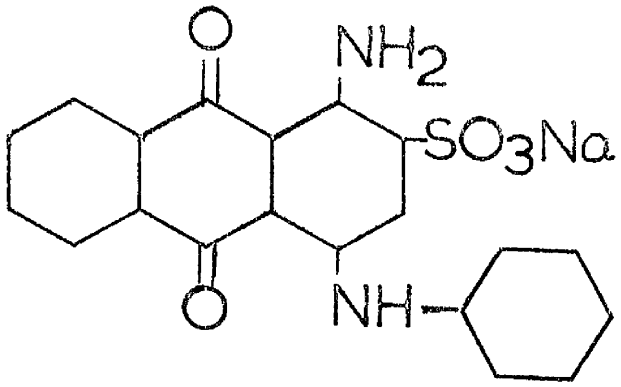
continuous running. The lamp has a weak continuous spectrum as a background with a number of superimposed strong monochromatic bands, the five major emission lines in the spectrum of the lamp are at 3655A, 4047A, 4358A, 5460A, and 5780A.

Transparent film (nylon, polyester, Cellophane, etc.) was used throughout the present work. The degree of fading was measured as decrease in optical density of the dyed film at the wave-length of maximum absorption of that dye after exposure for a certain period of time. By the Lambert-Beer Law, for constant thickness of transparent medium, optical density varies with concentration in a linear manner provided that no change occurs in the absorption properties of the solute due to alteration in degree of association[85]. For the absorption spectra, readings were taken at intervals of 50A. It was observed that the optical density of the heavily dyed films (o.d. > 1.0) was difficult to determine accurately. For this, the differential analysis method was used[8], whereby one can read high optical densities with good precision. In place of the usual reference blank one of the dyed films of the same substrate dyed to a pale shade (o.d. 0.4 - 0.7)

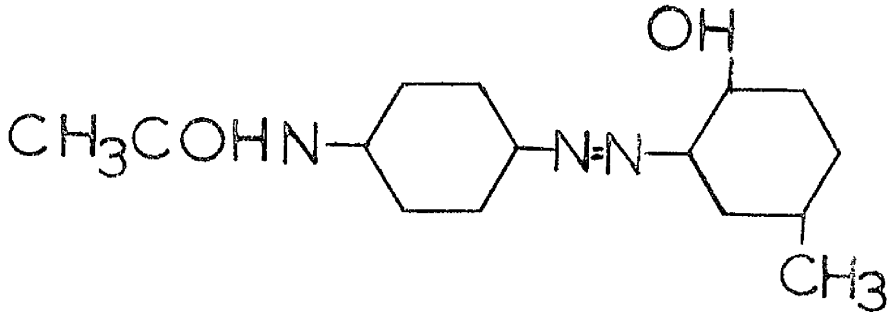
is used. The resulting optical density reading is then added to that of the coloured blank used. This gives the true value for the film under test, since optical densities are additive. The method has been reviewed by Giles and Shaw[84].

Dyes used in this part of the work

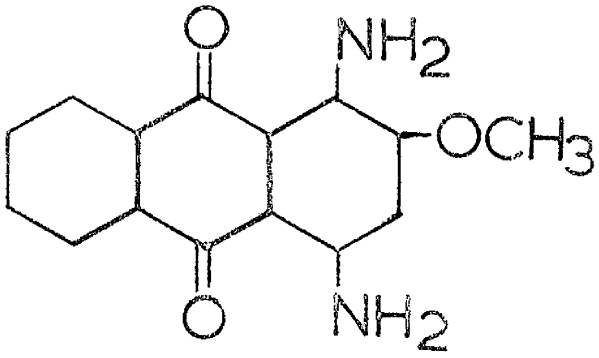
Solway Ultra Blue B (C.I. 62055)



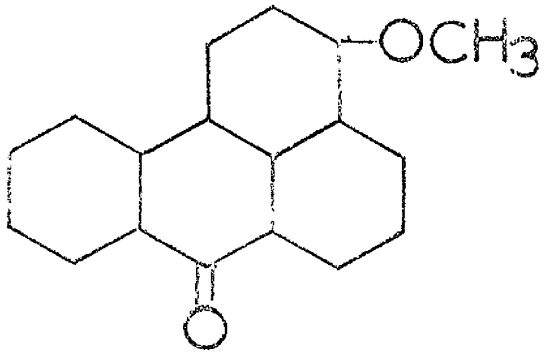
Dispersol Fast Yellow G (C.I. 11855)



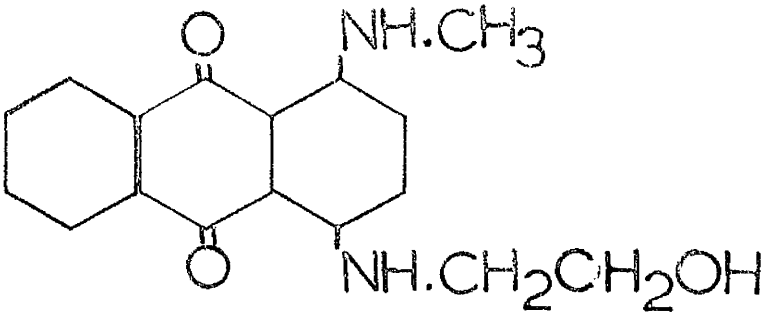
Serisol Brilliant Red X3B (C.I. 62015)



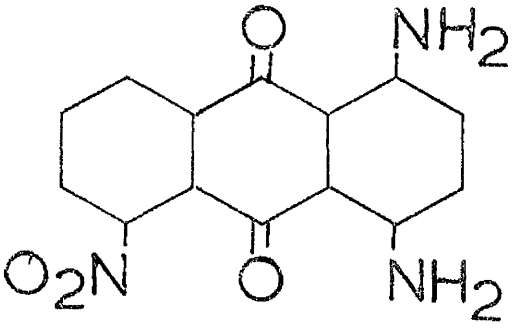
Duranol Brilliant Yellow 6G (C.I. 58900)



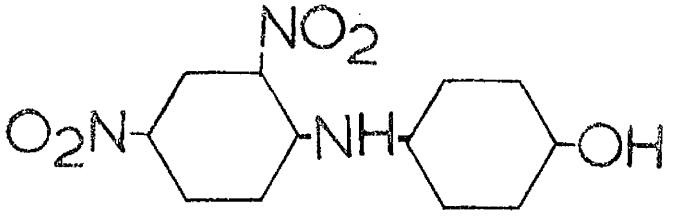
Serisol Brilliant Blue BG (C.I. 62030)



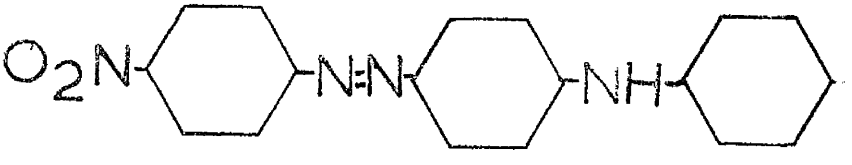
Duranol Brilliant Violet BR (C.I. 62030)



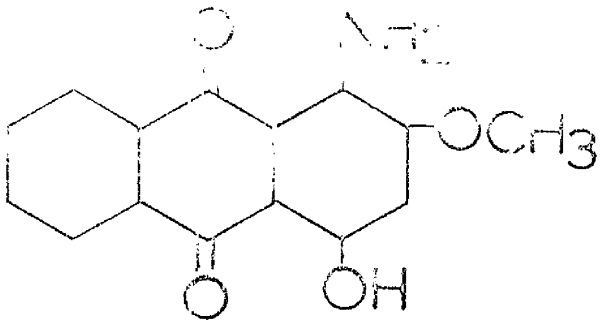
Dispersol Fast Yellow A (C.I. 10345)



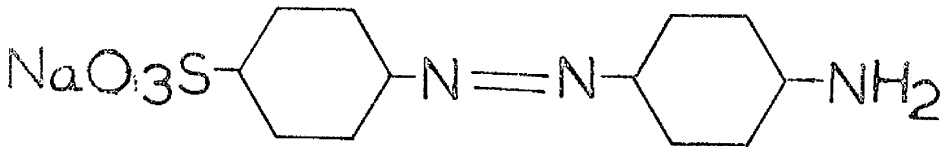
Dispersol Fast Orange A (C.I. 11080)



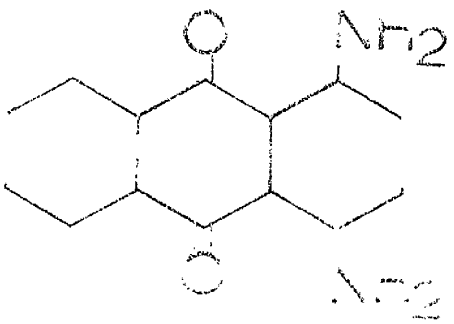
Celliton Fast Pink RF (C.I. 60755)



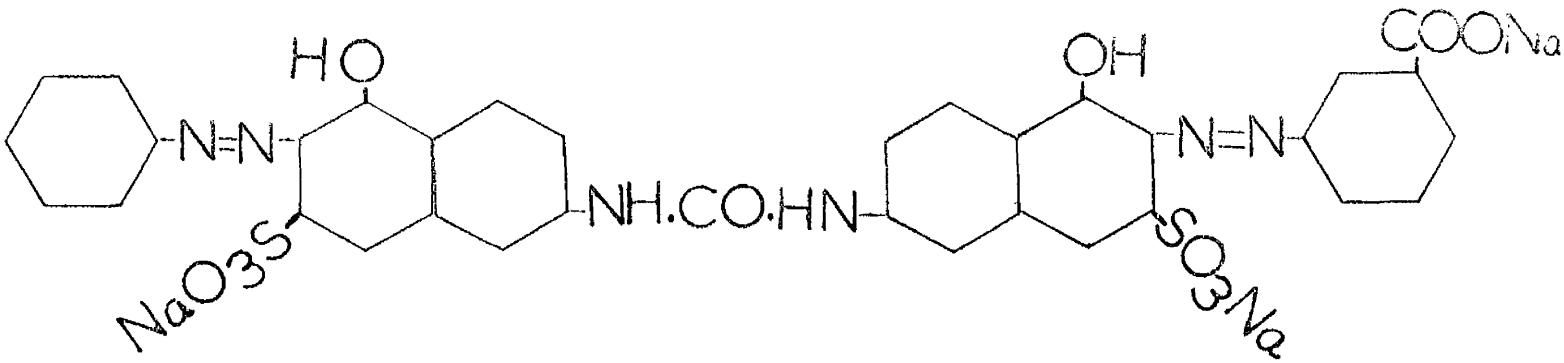
Durazol Orange 2G (C.I. 40215)



Duranol Violet 2R (C.I. 61100)



Direct Fast Orange WS (C.I. 29155)



Serisol Brilliant Green 3G. (Disperse dye-Mixture)

Substrates and methods of dyeing

Nylon: Transparent 0.003 in. nylon film supplied by I.C.I. was used. The film was cut to 3 ins. x 7 ins. and was wound on the glass frame as shown in (fig.2). The dyebath was prepared with 0.01gm. disperse dye and 0.5gm. dispersing agent (Lissapol N., I.C.I.). The material: liquor ratio was kept at 1:800. The glass frame, and wound-on film, was entered into the dyebath at 40°C and the film was rotated therein at 20r.p.m. by electric motor. A quite uniform dyeing was obtained by this method. The temperature of the dyebath was slowly raised to the boil and the dyeing was continued for 60 mins. The film was then removed from the dyebath, rinsed and dried in the oven at 30°C.

Polyester: It is well known that polyester fibres, because of their very compact structure, are difficult to dye. Two methods have been recommended for the dyeing to Terylene (I.C.I.) polyester fibre, viz. either dyeing at b.p. in presence of a carrier, or at high temperature (pressure dyeing). The carriers, generally used for dyeing of polyesters at b.p. are simply phenolic compounds and those containing hydroxy-groups have an adverse effect on light-fastness if used in dyeing[85-86].

Phenol acts as a disaggregating agent for dyes in solution[87] and in solid substrates[85] and 4-hydroxydiphenyl seems to disaggregate disperse dyes in polyester fibre. This reduces the light-fastness of the dye and hence the use of such carriers has to be avoided when tests on light-fastness are carried out. For this reason polyester film was dyed in a domestic pressure cooker using 15 lbs/sq.in. pressure (121.5°C.). Three different dyebaths were prepared with 0.01, 0.02 and 0.03 gm. of disperse dye respectively, and 0.5 gm. of Lissapol N. (I.C.I.) was added to each dyebath. The material: liquor ratio was kept at 1:500. Melinex (I.C.I.) polyester film portions each 0.5 gm. in weight were entered into the dyebath cold. The dyebaths were placed in the separators of the pressure cooker and dyeing was continued for 60 mins. at 15 p.s.i. The films were then removed from the dyebaths, rinsed and dried in an oven at 30°C.

Regenerated Cellulose film: Most of the regenerated cellulose films used were normal commercial Cellophane (thickness 0.001 in.). The dyeing method was similar to that used for nylon. The dyebath was prepared with 0.01 gm. of direct dye, and 20% (on the weight of film)

Glauber salt. Cellophane film mounted on a glass frame was entered into the dyebath at 40°C and the dyeing was continued for 60 mins. by raising the temperature of the dyebath gradually up to 85°C. The film was continuously rotated in the bath at 20 r.p.m., then it was removed, rinsed and dried in an oven at 30°C.

Gelatin: 6 gm. of pure photographic powder was dissolved in 100 ml. of water by raising the temperature of the solution gradually to b.p. When the solution had thus become clear and transparent, 3 ml. of the dye solution (i.e. 0.03 gm. dye) was added to the gelatin solution and mixture stirred vigorously. The film was then cast on "subbed" photographic glass plate of size 4 in. x 2in. on a screw-levelled platform. When casting, care was taken to obtain a uniform thickness of film. To protect from dust another glass plate was placed a little above the drying films. The films were dried by the heat of four carbon electric lamps underneath the plate. The lamps were switched off if the temperature of the glass plate rose above 40°C. Dried film was then

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"Subbing" refers to a treatment with a silicate solution, followed by drying, given to the plates used in this work (kindly supplied by Ilford Ltd.) to ensure the adhesion of the gelatin emulsion in subsequent processing.

cut to a size suitable for inserting in the cell carrier of the spectrophotometer. While preparing the slides for fading the film surface of cut glass was covered with another strip of glass of the same size and the ends bound firmly together by tape to prevent any movement in the event of the film peeling from the glass. Some inequalities in optical density due to drying irregularities were noted round the perimeter of the plates and consequently only the central portions of the plates were used for fading tests.

Preparation of film slides for fading

Preparation of film slides for fading

The dyed film (nylon, Melinex or Cellophane respectively) was cut to 1.0 x 5.0 c.m. and placed between two aluminium strips of the same size having an aperture in the centre, with an area of 1.2 cm^2. The slide thus prepared was quite suitable for direct insertion in the cell-carrier of the spectrophotometer. Prepared slides were placed firmly in the cell-carrier and it was found that there was no movement of slides while sliding the carriage to and fro in use.

Temperature control device

As the main purpose of this work was to study the

effect of high temperature on fading, a wide range of temperatures (60 - 110°C) was used. The heater used to obtain the required temperature is shown in (fig.32-33). This apparatus is based on one first described by Grant et al.[87a]. It consisted of nichrome resistance wire wound between the PTFE formers F_3 and F_2 in such a manner as not to obstruct the light beam traversing the ampoule The heating current was supplied from the a.c. mains through a transistor power supply unit. The terminals of each heater were connected to the two terminals of a voltmeter which was connected in series with an ammeter, as shown in the circuit diagram. The apparatus was constructed in the Departmental workshop. The temperature within each heater was calibrated for the known values of current using chromel-alumel thermocouple. By controlling the current passing through the resistance of each heater it was possible to adjust the required temperature to an accuracy of $\pm$ 2°C. Although the temperature of the laboratory did not vary to a great extent, care was tken to check the temperature of the heaters from time to time.

When the temperature in all the heaters was stable the prepared slides were inserted in the heater

through the slot (see fig.1A). These slides were taken out at different intervals of time during exposure and the degree of fading was determined in the manner described. In most cases the reading of o.d. were taken until there was ca. 50% loss of colour.

Fading under dry and wet conditions

To study the effect of fading at high temperatures of completely dry or wet conditions the above described method was slightly modified. Tests were made only at two different temperatures, 63°C and 100°C. In order to obtain complete dryness, granules of calcium chloride were placed in a cylindrical "Pyrex" glass cell, while 20-30 c.c. of water was placed in another "Pyrex" glass cell, for humidification. The heaters in which the slides for fading were placed were inserted in these tubes, which were stoppered. The whole unit was then exposed to the fading lamp and fading was measured as usual.(fig.1A and 1B).

EXPERIMENTAL

PART II -- QUANTUM EFFICIENCY OF FADING

It has already been stated that one of the main difficulties in determining the quantum efficiency of fading of a solid lies in measuring the amount of light falling on the surface of the solid. Generally a calibrated thermopile is used to measure the light falling on the exposed surface. The main disadvantage of this method is that it is laborious and not very reliable.

Efforts have been made in the past to replace such a physical method of measuring the light by a chemical method. In spite of the proposals for using many substances as chemical actinometers, made from time to time, there is still an obvious need for an actinometer capable for measuring small doses of ultra-violet light of both short and long wave-lengths. The simplicity and advantages of the widely used uranyloxalate actinometer have been described by Leighton and Forbes[88-89]. The main disadvantages of this actinometer are that it requires a very long time of exposure, and is not very sensitive. It was found however, that the sensitivity could be increased by using a dilute solution, but this would require a longer time of exposure. Parker and Hatchard[90-91] later made a

detailed study of the characteristics of this new chemical method. They used potassium ferrioxalate in place of uranyloxalate. Parker[92], had covered the wave-length range of 2537-4800A° and found that in this range the quantum efficiency of ferrioxalate is unity. Thus the wide range of wave-length covered makes the actinometer suitable for polychromatic photometry. On exposure to this light ferrioxalate ions undergo decomposition according to the equation,

$$2[Fe(C_2O_4)_3]^{3-} \rightarrow 2\ Fe(C_2O_4) + 3[C_2O_4]^{2-} + 2\ CO_2$$

Allmond and Webb[93] further found that 0.006M. ferrioxalate in 0.1 N sulphuric acid could be photolysed to complete decomposition without precipitation of ferrous-oxalate.

Measurement of dye concentration on the film

The concentration of the dye in the transparent film was determined as follows. Several pieces of transparent film, each 0.5 gm. in weight, were dyed in test tubes to different depths of shade. The dyeing was continued for one hour at b.p. and 85°C for nylon and Cellophane, respectively. After determination of the optical density of each dyed film the dye from the film was extracted with 20 c.c. of dimethylformamide.

In some cases heat had to be applied in order to remove the dye completely. The dye was extracted by constant shaking by an electric shaker. The optical densities of the films were determined again after extraction to ensure that the dye was stripped off completely. The resulting extracts were then diluted to 50 c.c. in standard flasks and the optical density of each solution was determined by use of the Unicam SP 600 instrument, and the dye content readily found from a calibration graph.

Measurement of light

As stated above, the ferrioxalate chemical actinometer was used for this purpose. Two different concentrations of ferrioxalate solution were made, depending upon the wave-length of the light used for fading.

It has been found that when light of wave-length up to about 4300A is to be measured, a 0.006M solution of ferrioxalate can be used quite conveniently. For longer wave-lengths a 0.15M solution is more convenient. The 0.006M actinometer solution was prepared by dissolving 2.947 gm. of potassium ferrioxalate (commercial quality crystals) in 800 c.c. of water. 100 c.c. of 1.0N -

sulphuric acid were then added and the solution was diluted to one litre. The 0.15M solution was made in a similar manner, using 73.68 gm. of ferrioxalate crystals. As the actinometer solution is very sensitive to light, the entire preparation of the solutions was carried out in a dark room with illumination by Kodak OB safelight filter and the solution was stored in the dark throughout the experiment.

Two sets of experiments were carried out as follows: (a) In the first set 30 ml. of the actinometer solution were placed in a 4 cm. fused glass spectrophotometer cell, with the front face normal to the radius from the lamp, and covered with black paper except for an aperture of 1.2 $cm.^2$ cut in the centre (some apparatus are shown in fig. 33). A film slide was prepared by making a sandwich of undyed film in between two aluminium strips having an aperture of area 1.2 $cm.^2$ in the centre. This slide was placed carefully in correspondence with the aperture of the cell. Four Chance all-glass filters were used to separate the regions of the spectrum of the mercury vapour light (Osira 400w. lamp). The transmission curves of the filters are shown in (fig.5).

After the slide was mounted on the cell, one of

these filters was placed on it and the whole unit was then inserted in a specially constructed brass box, closed on the other three sides. This box was placed on the inside of an annular casting of aluminium sheet 15 in. high and 17 in. diameter surrounding the lamp placed vertically. The box was placed at a distance of 8 in. from the arc of the lamp. The air temperature near the cell during exposure was 63°C. The actinometer was exposed for 30 min. The cell was then removed and kept in the dark and the decomposed solution was titrated against a standard solution of ceric sulphate.

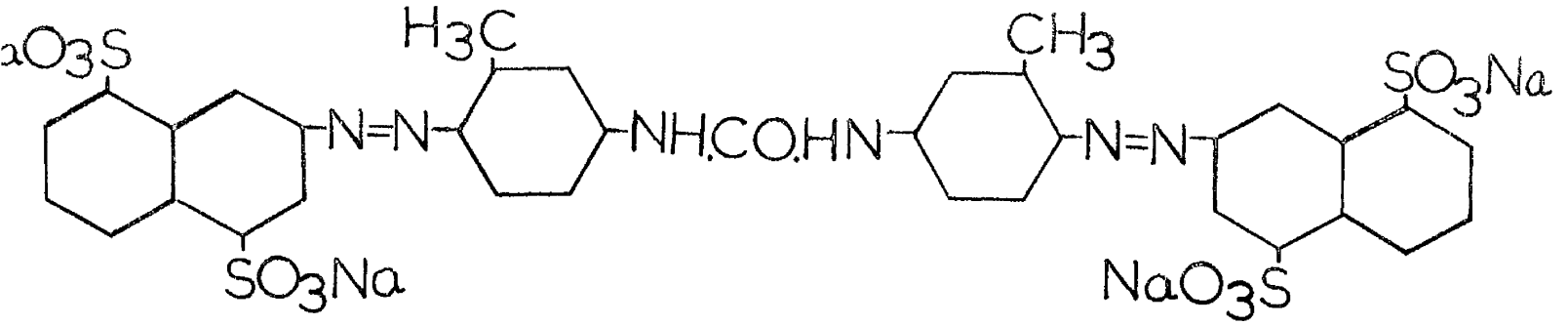
(b) A similar experiment was carried out but this time the slide of undyed film was replaced by a dyed film and the cell was exposed for 30 min. under exactly identical conditions. The decomposed solution in this case was again titrated against a standard solution of ceric sulphate using N-phenylanthranilic acid indicator. These experiments were repeated using all four filters and the quantum efficiency data calculated from the difference between titres for solutions behind dyed and undyed films. The amount of dye decomposed was calculated from the difference in o.d. of the film before & after fading.

During the experiment the temperature of the actinometer solution was found to be 46°C. To

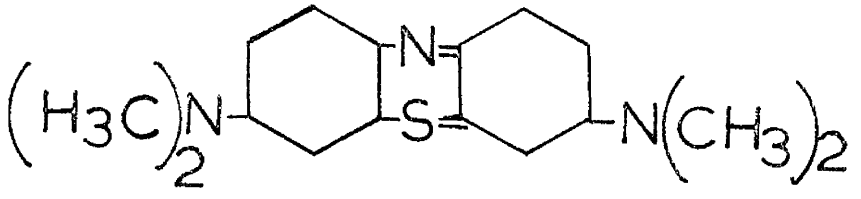
eliminate any effect of heat on the decomposition of the actinometer solution, another cell with the same amount of actinometer solution (30 c.c.) was exposed side by side under exactly identical conditions except that the aperture of the cell was covered with black paper and thus the light was prevented entirely from falling on the actinometer solution. After 30 min. the decomposed solution was titrated as before. This value of titration reading was subtracted from one obtained when light was allowed to fall on ferrioxalate solution through the aperture of the cell.

Dyes used in this part of work

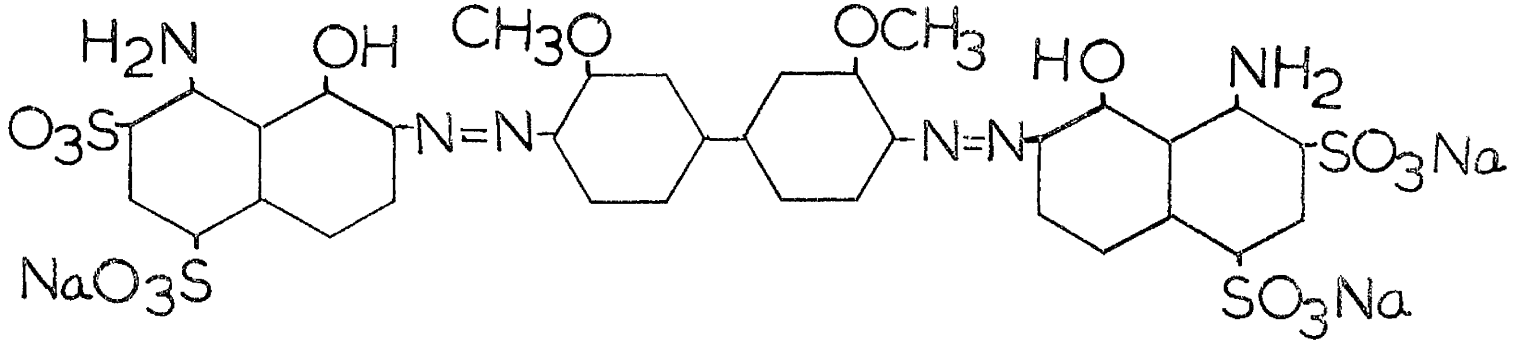
Calcodur Yellow RL (C.I. 29025)



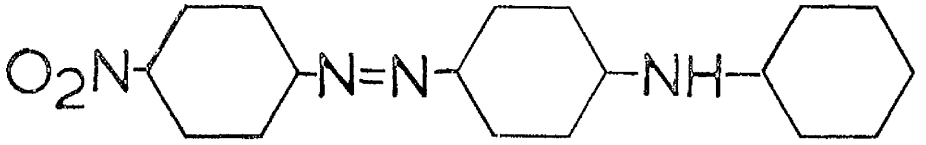
Methylene Blue BP (C.I. 52015)



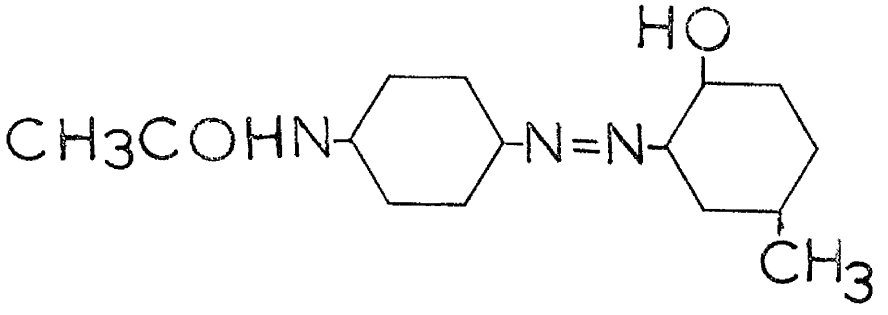
Chlorazol Sky Blue FF (C.I. 24410)



Dispersol Fast Orange A (C.I. 11080)



Dispersol Fast Yellow G (C.I. 11855)



Purification of the dyes

Two types of dyes were used in this section of the work, viz. disperse and direct dyes. All the dyes of each class were purified before applying them to the films.

All direct dyes were purified by the precipitation method. 5 gm. of the dye was dissolved in hot water and then precipitated by adding a concentrated hot solution of sodium acetate. The dye was filtered off and redissolved and again precipitated by adding more concentrated hot solution of sodium acetate. This procedure was repeated at least five times with more and more concentrated solution of sodium acetate each time. The sodium acetate was next removed by repeated extraction of the dried product with hot ethanol.

All disperse dyes used were purified by Soxhlet extraction with benzene.

The process was continued for 4-5 hours. The bulk of the liquid in the flask was then reduced to half by distilling off some of the solvent. The extracted dye was then crystallised by placing the flask in an ice-bath. The crystals of the dye were collected carefully and dried in an oven at 30°C.

The purity of dye was tested by thin-layer chromatography.

EXPERIMENTAL

PART III: STASTICAL RELATION BETWEEN MOLECULAR GEOMETRY OF DYES AND THEIR LIGHT-FASTNESS

This work was a continuation of that already carried out by the author's colleague N.B. Shah. As suggested by Baxter et al.[4-11-94] there is a relation between the degree of aggregation of dyes in the fibre and their light-fastness. Holt and Sadler[95-77] have shown that there is also an apparent relation between the symmetry of substitution of groups in aromatic molecules and their crystal lattic energy, revealed in their water solubility and behaviour in adsorption by some substrates. Since the degree of aggregation is expected to be related to molecular weight and also to lattic energy, it follows that a relation between molecular weight or molecular symmetry of dyes and their light-fastness in a fibre might be expected.

The data for all the dyes in the Colour Index[96] for which constitution and light-fastness are given were examined. For simplicity all those having planar or nearly planar molecules, were selected for statistical analysis. All the light-fastness data are the British (B) or continental (C) gradings for normal shade depths taken from the Colour Index. For the measurement of molecular axial ratio of all the dye molecules selected, Catalin (stuart type) molecular models were used[97]. The "molecular

RESULTS AND DISCUSSION

PART I - INFLUENCE OF TEMPERATURE AND HUMIDITY ON FADING

axial ratio", x/y, of the dye molecule is defined as that of length (x) to breadth (y) of the smallest rectangle enclosing the molecular model. All markedly non-planar dyes were excluded, because non-planarity introduces uncertainty in the measurements used. Most of the results did not show any significant relation between light-fastness and axial ratio. It was considered that results not significant might be affected by the fact that increase in the molecular weight of dye often increases the axial ratio. The molecular axial ratios of all dyes were then divided by the respective molecular weights and the data were electronically computed to find if there was any significance in the relations. The results of both the series of tests are shown in table XI - XVI and in (figs. 34-39).

Significance of slope of fading curves

It has been pointed out from time to time that the fading reaction involves oxygen and/or water vapour and therefore it can be assumed that both the size and the nature of the air-dye interface may have considerable influence on this reaction. The smaller the surface area exposed the less will be the fading. If the dye is aggregated in the substrate then a smaller area of dye will be exposed. It is suggested by Baxter et al.[11] that fastness is at least partly determined by the physical form of dye in the substrate, thus dyes of higher fastness are more likely to be highly aggregated than those of low fastness, though this is of course not a universal rule. It is sometimes possible to determine qualitatively the state of dye by examining the slope of fading rate curves. In normal practice, five types of fading rate curves can be obtained as shown in (fig.42).

In (fig.42) I represents a first (a) or second order reaction curve. This case (a) occurs when the rate of fading decreases exponentially with time . This type of curve indicates that the dye is either molecularly dispersed or present as very small aggregates. Harashima et al.[98] have observed that some direct cotton dyes fade according

to a second order law (linear relation between time and reciprocal of optical density, or nearly constant curvature of the graph of O.D. against time). A possible cause of this type of fading curve might be that low moisture content of the substrate is responsible for retarding the rapid fading of molecularly dispersed dye. A zero order curve in which the rate remains constant with time is obtained when the total area of the dye exposed to air, moisture and light remains constant throughout. But this type of situation rather seldom occurs in practice(fig.42III).

In practice the most widely occuring fading curve is that of type II (in fig.42). In this case the dye is partly molecularly dispersed and partly present as large aggregates. The molecular dispersion gives the initial rapid fade (first-order) and the aggregates give the subsequent constant rate of fade (zero order). The curve of type IV in (fig.42) has initial negative fade, i.e. dye concentration appears to increase (increase in o.d.) during the initial period of exposure. This may be due to the break down of the aggregates in the heat of illumination, and indeed the effect can be produced by heat alone. This is probably the most definite evidence of the presence of aggregated dye particles.

The fading curves obtained with polyamide and polyester substrates (oriented) during this work are of type I, the rate of fading decreasing exponentially with time. The results are represented by the graph of time against $\log\left(\frac{O.Do}{O.Dt}\right)$ which give straight lines, a characteristic of first-order reaction, for all the dyes used, as shown in (figs. ~~6 to 28~~). (figs. 6, 8, 10, 12, 14, 16, 18, 20, 21,)

O.Do = Initial optical density

O.Dt = Optical density at time (t)

The two main features of these graphs are - (a) the nature of the reaction seems to remain the same throughout, at all the temperatures used; (b) as the temperature increases the slope of the line increases, i.e. rate of fading increases with temperature.

Sensitivity of fading to humidity and temperature

The results obtained in this work for fading at high temperatures of dyes on polyamide and oriented polyester substrates show quite an opposite effect to what is generally observed withhydrophilic fibres, where rate of fading decreases with increase in temperature. The cause of the effect obtained with hydrophilic fibres has quite reasonably been explained as increasing loss of moisture

with rise in temperature, but if so, the opposite effect obtained with hydrophobic fibres seems to be anomalous. The true meaning of the results of Hedges[20], McLaren[40], and Cunliffe[25], each of whom showed that high humidity gave an increase in fading rate is not really as clear as appears at first sight. It might appear to be a simple mass action effect, i.e. in the fading reaction water is an essential component and therefore fading rate rises with water concentration. But if this were so the effect would be similar for all dyes in each fibre, which it is not. Further whatever may be the reaction mechanism, the amount of water required[24] for fading must be very very small compared to the moisture content of the dyed sample.

In this work the dyed disoriented polyester films were exposed under two different conditions, viz. at R.H. ca 100% and dry, in both cases at 100°C. Examination of the fading curves (Fig. 27-28) obtained under these conditions shows that, unlike effects obtained with hydrophilic fibres, the difference in fading rate is not so noticeable.

Diffusion-restriction effect

With a highly crystalline fibre structure, e.g. in polyacrylonitrile or polyester fibres, the flow of water vapour molecules is hindered by the very compact internal structure of the fibres, and it has been suggested[4] that this retards the diffusion of water vapour molecules towards the dye fading site. On this view the fading rate of any given dye-fibre system will depend upon the rate at which water molecules can pass through the substrate in the region of the dye molecules. This retardation of diffusion of moisture, occuring in the hydrophobic synthetic fibres, has been named by Giles[4] as a "diffusion-restriction" effect. At normal temperature this effect may be expected to be marked, but the present results of fading at higher temperature seem to show that it may become less important with rise in temperature, probably because of some change in the internal structure of the fibre. When the polymer substrates are heated above their glass transition temperature the specific volume of the polymer increases and the segments of the polymer chain are thought to "thaw" out sufficiently to begin to permit rotation about the long axis of the molecule. Studies in the density-temperature relationship

of polyethylene terephthalate have shown that[99] an increase in temperature from 40° to 100°C. produced an increase of 2.7 and 1.3 percent respectively in the volumes of the amorphous and the crystalline polymer.

Due to this volume expansion the polymer chains move away from each other and thus the space between them increases. This situation should help water vapour and oxygen to reach the fading sites, i.e. the dye molecules trapped in between the polymer chains. This could be the reason for the more rapid fading at higher temperatures. Another explanation is that any dye aggregates present are broken down, thus exposing more surface to oxygen, but this is anyway believed to occur to some extent in the early stages of fading in many systems. It is believed that dye in polyester substrates is molecularly dispersed[78]; though some dye aggregates may also be present. The author believes, though, that it is not likely that breakdown of aggregates is the cause of the high temperature effect with hydrophobic fibres. It may be that water molecules which are attached to dye molecules by hydrogen bonds, protect the dye from oxidation by atmospheric oxygen. When this hydrogen-bonded water is lost the dye molecules become susceptible

to oxidation; this could occur when the total water content of the fibre becomes too low to permit adsorption of at least one water molecule by each accessible polar group in the fibre and the dye. The evidence in support of this hypothesis has been given by research into the stability of dehydrated food-stuffs. Salwin et al.[100] showed that there is an optimum moisture content for the stability of such dried products. This optimum corresponds with the amount of water calculated from the adsorption isotherm by the BET equation; required to form a monolayer on the total surface of the solid. It is supposed that at the monolayer stage each polar group in the solid is protected from attack by atmospheric oxygen by its attachment to a water molecule. When the last traces of water are removed oxidation can occur. Thus the author suggests that a similar process could occur in very dry fibres.

Effect of ultra-violet light on light-fastness of Terylene polyester fibre

Light-fastness data of certain disperse dyes on Terylene polyester fibre show that some dyes are of considerably higher fastness to daylight exposure than to Fade-Ometer. This is not due to high humidity condition

in Fade-Ometer since the effective humidity was 0-5%[101]. It is possible that this low light-fastness in Fade-Ometer is due either to excess of ultra-violet light or to a higher temperature in the Fade-Ometer.

Two dyes[102], one having the same light-fastness in daylight and in Fade-Ometer and another having different fastness, were selected. Both the dyes were applied to Melinex (I.C.I. polyester) film as described in the experimental section, and were faded in the apparatus shown in (fig.1). In order to cut off ultra-violet light special Chance glass filters were used. Two film slides, one with filter and one without, for each dye, were faded and fading curves were plotted from the results obtained (fig. 25,31). It is clear that the slide which was exposed under the filter did not fade as much as the other, exposed without filter. Some fading however did occur with the slide exposed with filter. This might be due to the heat of the fading lamp.

Fading rates of direct dyes on Cellophane, and an acid dye on gelatin at two different temperatures and humidities were examined (fig.22,29,30). In these cases the graphs of optical density against time show at first a sharp fall and in fact fading occurs according to

first-order. It slows down to show a zero order fade. The rate of fading in dry conditions is much slower at 100°C than at 65°C. These results are quite in agreement with the assumption made earlier[102]. Hedges[20] found approx. 75% greater loss of colour (Soluble Blue) at 50°C than at 10°C., the regain being 18% in both cases and the time of exposure the same. Thus the degree of separation of the 10°C and 50°C tests in Hedges results and of those at 65°C. and 100°C. in this work show that temperature is an important factor in determining fading rate.

As stated above, a straight line relation was found for each temperature when the values of $\text{Log}(\frac{O.Do}{O.Dt})$ were plotted against time. The slope of these lines was then calculated and the respective values of log k were determined. A straight line relation was obtained when the values of log k were plotted against 1/T the reciprocal of the absolute temperature. The values of energy of activation of fading for all the dyes used were then calculated from the slope of these last-mentioned lines. From the values mentioned in Table IX it is clear that the values of activation energy for fading on nylon are in all cases much higher than those for fading on polyester.

This suggests that more bonds have to be broken in nylon than in polyester before fading can occur. It is difficult to understand how these extra bonds in nylon can be dye-substrate bonds, but they might be dye-dye bonds, i.e. the dye may be more highly aggregated in nylon than in polyester because of the less crystalline structure of nylon, which could allow the growth of larger aggregates. Indeed, in polyester the dye may well be largely mono-disperse in very small aggregates such as dimers. The extra energy required in nylon would be needed to breakdown the aggregates. This hypothesis requires a good deal of extra experimental work to check its validity, but it might reveal an interesting new method of examining the structure of adsorbed dye in substrates.

RESULTS AND DISCUSSION

PART II - QUANTUM EFFICIENCY OF FADING

Sensitising action of dyes

Photolysis of fibre macromolecules, e.g. cellulose, silk, or nylon, will occur only when light is absorbed of sufficiently high energy to break the chemical bonds in the molecule. The amount of visible light absorbed by the undyed fibre is almost nil, and the rate of degradation is extremely low, except in presence of catalytic sensitisers, e.g. specific dyes, zinc oxide or titanium dioxide. One of the most important features of the degradation of dyed textile material by visible light is the property possessed by many dyes of acting as such catalytic sensitisers, and thus of accelerating the rate of degradation of fibre. This they do by absorbing radiation in the near ultra-violet and visible region of the spectrum and making the absorbed energy available for the degradation of fibre.

The initial process responsible for the tendering of the fibre in such cases, or the fading of dyes, is the absorption of light by the dye molecule. As a result of this absorption of light energy one of the electrons in the dye molecule is raised to a higher energy level. The molecule is then said to be "excited". This excited molecule returns to the normal ("ground")

state when the energy acquired is rapidly degraded to heat. The short life normally shown by the excited state of the dye molecule prevents it from having time to transfer its energy to other molecules colliding with it. Such dyes, when applied to textile fibres, do not accelerate fibre degradation. The fluorescent dyes however have been found to accelerate degradation. In these dyes the excited molecule can remain in the excited state for a longer time without losing its absorbed energy as heat. The return to the normal state results in emission of light as fluorescence. The excited dye molecule can also return to the normal state as a result of collision, thereby transferring the absorbed energy to the molecules which collide with it. In the dye-substrate system, when the excited dye molecule returns to the normal state the energy absorbed by dye can be passed on either to oxygen molecules (from the air) or to the substrate itself.

Fading and its relation to the absorption maximum of the dye

As stated earlier (P 21) it is very difficult to determine which part of the spectrum is most responsible for fading of any given dye. Thus whereas Morton[53]

considered that the greater part of the fading is due to a narrow band of wave-lengths near the maximum absorption of the dye, Appel and Smith[42] obtained results which did not confirm this belief, from tests on fading rate of certain dyes exposed behind coloured filters. In fact they found that certain blues were not in fact faded by light of wave-length corresponding to that of maximum absorption and they concluded that the colour of the dye is not a safe guide to the spectral region causing fading. It seems possible however that the results obtained by Appel and Smith may have been rendered uncertain by rather broad transmission bands of the glass they employed. It has been suggested[53] that if only monochromatic light is considered then the conclusions reached by Norton may be justified. Rather confusing evidence in this matter has also been provided by Bleisdell[104]. He exposed films of cellulose triacetate and of Terylene polyester material, dyed with disperse dyes, to the 250-watt Uviarc lamp, for which the emission intensities at 3030, 3130, 3650, 4050, and 4350A respectively are similar. Yet the fading produced by radiation at 3030 and 3130A was far more than that at 4050 and 4350A. If such comparisons are to be significant for substances having

relatively broad absorption bands (as in the case of many dyes) a more satisfactory comparison would be between the quantal energies associated with the different wave-lengths and the rate of destruction of the dyes.

McLaren[80] exposed the light-fastness standards (Nos. 1-7) to daylight and found that with increase in fastness from 1-7 the effectiveness of the long-wave region of daylight decreases and that of the short-wave region increases. He also found that standard 6 absorbs light more strongly above 6000A than standard 3 does, yet it was not faded at all by radiation above 6000A. It seems that the effectiveness of different spectral regions, in fading, may be independent of the absorption characteristics of the dye, but it may be dependent on the energy absorbed over the broad absorption waveband.

The quantum efficiency obtained for Chlorazol Sky Blue FF fading is higher with the yellow filter than with the green filter (Table X). This agrees with McLaren's findings since the dye is a fugitive one.

From an examination of the absorption curve of the film dyed with Durazol Rubine B (fig.4) and the transmission curves of the filters (fig.5), it might seem

that the amount of fading and the quantum efficiency would be higher with the yellow filter than with the green, but it is not. A similar situation occurs with solutions of cobaltioxalates[105]. These show two absorption bands at 6050 and 4260A, respectively but they are decomposed photochemically only by light at 4260A.

From the results obtained in this work and those reported earlier[57-58] it is clear that the quantum efficiency of fading of dyes in solution is much higher than on textile fibres. This might be due either to the more ready dissipation of energy by kinetic action of the excited dye molecules in solution, or to the greater degree of aggregation of the dyes in the solid adsorbed state, or to both causes together. There is at least one example in the literature[34] where the quantum efficiency of the photo-reaction of dyes at an electrode was found to be much higher than for fading in solution. The results were attributed to the low electrical impedance of the circuit enabling the hydrogen atoms to be removed as fast as they could diffuse to the electrode. In the same work it was also found that within any one absorption band of the dye the quantum efficiency of photo-reaction was independent of the wave-length.

It remains to be explained how the quantum efficiency of fading on a fibre can be so extremely low, even for dyes which would be expected to be largely monodisperse (e.g. Sky Blue FF) and therefore not protected from photo-decomposition by association. It must be admitted that no very satisfactory explanation can be given. The absorbed radiant energy is clearly being readily dissipated mainly as heat, but in some cases possibly by degradation of the substrate, as in catalytic tendering of cellulose, but in these cases it seems that the degradation is a secondary action due to hydrogen peroxide generated by the excited dye molecule. Eyring[49] states that photo-decomposition is likely to be more difficult in a crystalline substance than in one that is gaseous or dissolved. Possibly even very small associated particles e.g. dimers or trimers may decompose much less readily than monodisperse molecules, and if we then assume that all dyes in fibres are associated to some degree at least as far as the dimeric state, this might offer a partial explanation of the effect.

RESULTS AND DISCUSSION

PART III -- STATISTICAL RELATION BETWEEN MOLECULAR GEOMETRY OF DYES AND THEIR LIGHT-FASTNESS

This investigation was made to examine the working hypothesis that with shortening of the longest molecular axis of dye light-fastness is increased, by either (a) the number of possible points of attack by an oxidising agent being decreased; or (b) the crystal structure being strengthened. The cause of any relationship between molecular geometry of dyes and their light-fastness could thus be either physical or chemical in origin. It is obvious that photochemical attack can occur at more points simultaneously, if there is an increase in the length of conjugate chain in the molecule. The effects (a) and (b) are difficult to examine independently because dyes in the fibre are probably present both in monomolecular dispersion and as aggregates. Thus effect (a) is likely to be masked by effect (b).

Jeffreys[106] found that certain cyanine dyes in methanol solution fade more rapidly with increase in length of the polymethin chain. Since these dyes would be entirely non-associated in methanol, the observed effect can only be due to the chemical cause (a). In the present work, the molecular axial ratio and light-fastness grade for a variety of dyes were plotted. The main groups included in the investigation are direct dyes on cotton,

anthraquinone and azo acid dyes on wool, and anthraquinone vat dyes on cotton. Statistical analysis of the data of anthraquinone vat dyes shows a significant relation between symmetry of shape of these dyes and their light-fastness on cotton. The regression line accounted for 26 percent of the total regression. Thus the statistical analysis shows that geometrical shape of the dye molecule is one factor influencing the light-fastness. Any similar relation is difficult to detect for acid wool and direct cotton dyes because they are available in only a limited range of molecular axial ratios. Under these circumstances the chemical nature of the substituent groups rather than the molecular axial ratio is clearly the main determining cause of difference in fastness.

Apart from the axial ratio, which as stated may influence aggregation, molecular weight certainly does so, and it was thought that the independent influence of molecular weight might be eliminated from the regression by dividing the value of molecular axial ratio for each dye by its molecular weight, and plotting the values so

In this test only dyes with planar molecules were included, to avoid an extra variable.

obtained, against light-fastness. Unfortunately this procedure did not increase the significance of the data.

Relation between molecular geometry of dyes and fading in different wavebands

As mentioned in Part II of this thesis, McLaren[60] found that fugitive dyes are mostly faded by the longer visible wavebands and those high fastness by the shorter wavebands of blue, violet and ultra-violet light. On the assumption that this relation might in some way be related to the symmetry of the dye molecule, the molecular axial ratios of dyes used by McLaren were plotted against the fading cause by blue-red region of the spectrum (fig.40). The statistical analysis showed very significant relation. From the graph it is seen that the percentage fading caused by the blue-red region increases with increase in axial ratio. McLaren's discovery takes no account of the relative quantum efficiency of the different wavebands.

One possible cause of the relation now revealed is that a small axial ratio, in some way not yet understood, favours a high degree of aggregation and that this in turn requires short-wave radiation to break it up, but it should be noted that the points on this particular

graph represent dyes of widely different chemical constitutions, and there is some tendency for the various constitutions to be grouped together.

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APPENDIX

Statistical Analysis of Results presented in Part III

I. Relation between molecular axial ratio (x/y) - molecular weight and light-fastness of anthraquinone vat dyes on cotton (Fig. 36. Table XIV)

$n = 50$, $(x - \bar{x})^2 = 75.1194$, $(y - \bar{y})^2 = 49.745$

$(x-\bar{x})(y-\bar{y}) = 20.5872$

$\bar{x} = 4.2344$, $\bar{y} = 6.510$

$b = 0.27406$

Source of variance	Degree of freedom	Sum of square	Mean square
(1) Due to regression	1	5.644	5.644
(2) About regression	48	44.101	0.91881
(3) Total	49	49.745	

$$F = \frac{5.644}{0.91881} \text{ with } N_1 = 1 \text{ and } N_2 = 48$$

$$= 6.144.$$

Therefore straight line accounts for 11% of total regression.

II. Relation between light-fastness and anolnic weight (Fig. 38. Table XV)

$n = 47$, $x = 20101$, $y = 199$, $xy = 87586.5$,

$x^2 = 8917201$, $y^2 = 919$

$b = 7.7344 \times 10^{-3}$

$y = 7.7344 = 10^{-3} \; x + 0.9262$

Source of variance	Degree of freedom	Sum of square	Mean square
(1) Due to regression	1	19.1659	19.1659
(2) About regression	45	57.2596	1.2724
(3) Total	46	76.4255	

$F = 15.06$ with $N_1 = 1$ and $N_2 = 45$

Therefore the straight line is highly significant for the regression and accounts for 25% of the total regression.

III. Relation between molecular axial ratio and light-fastness of anthraquinone vat dyes on cotton

(Fig. 39, Table XVI)

$n = 50$, $x = 104.84$, $y = 325.5$, $xy = 668.355$,

$x^2 = 235.2016$, $y^2 = 2168.75$

$b = -0.92066$

$y = -0.92066X + 8.4404$

Source of variance	Degree of freedom	Sum of square	Mean square
(1) Due to regression	1	13.0304	13.0304
(2) About regression	48	36.7146	0.7649
(3) Total	49	49.7450	

$F = 17.3$ with $N_1 = 1$ and $N_2 = 48$

Therefore the straight line is highly significant for the regression and accounts for 26.19% of the total regression.

IV. Relation between effectiveness of blue-red spectral region in causing fading and molecular axial ratio of dyes with planar molecules (Fig. 40. Table XVII)

$n = 31, \quad x = 62.46, \quad y = 1075.0, \quad xy = 2505.42,$

$x^2 = 134.8504, \quad y^2 = 6188.5$

$b = 37.7037$

$y = 37.7037X - 41.289$

Source of variance	Degree of freedom	Sum of square	Mean square
(1) Due to regression	1	12799.2016	12799.2016
(2) About regression	29	11807.5725	407.1576
(3) Total	30	24606.7741	

$F = 31.4$ with $N_1 = 1$ and $N_2 = 29$

Therefore the straight line is highly significant for the regression and accounts for 52% of the total regression.

Table I: Fading data for Disperool Fast Yellow G - on nylon

Exposure (Hrs).	Optical Density (O.D.) x 10^2	$\text{Log}\frac{O.D_0}{O.D_t}$ x 10^4	Temp.
0	42.5	0	
5	41	156	
8	40	209	
12	37	602	100°C
30	32.5	1165	
37	30.5	1441	
0	71	0	
3	69	125	
5	68	188	
14	65	384	90°C
19	64	417	
39	54	1189	
0	74	0	
8	70	241	
28	67	431	
35	65	563	
51	60	910	80°C

Table I: Continued

Exposure (Hrs)	Optical Density (O.D.) $\times 10^2$	Log $(\frac{O.D_0}{O.D_t})$ $\times 10^4$	Temp.
0	53	0	
3	48.5	386	
6	46	615	
9	44	808	
14	42	1011	110°C
20	35.5	1741	
23	34.5	1865	
39	24	3441	

Table II. Fading data for Serisol Brilliant Red X$_3$B on nylon

Exposure (Hrs)	Optical Density (O.D.) x 10^2	Log $(\frac{O.D_0}{O.D_t})$ x 10^4	Temp.
0	81	0	
4	78	164	
8	75	334	
27	50	2095	
35	35.5	3585	102°C
49	27	4771	
79	25.5	5020	
102	25.5	5020	
0	68	0	
4	66	150	
8	65	196	
27	61	472	
35	57	766	
49	53	1082	
79	44	1890	
102	39	2414	85°C
0	75	0	
27	71	238	
35	69	363	
49	66	556	76°C
79	59	1042	
102	55	1347	

Table II: Continued

Exposure (Hrs)	Optical Density (O.D.)	Log $\left(\frac{O.D_0}{O.D_t}\right)$ x 10^4	Temp.
0	78	0	71°C
27	77	56	
35	73	288	
49	69	533	
79	64	859	
102	61	1068	
0	78	0	63°C
4	77	56	
35	73	288	
49	71	408	
79	68	596	

Table III: Fading data for Colliton fast pink RF on Terylene

Exposure (Hrs)	Optical Density (O.D.) x 10^2	Log $(\frac{O.D_0}{O.D_t})$ x 10^4	Temp.
0	35.5	0	100°C
4	35	61	
34	33	317	
41	31.5	519	
93	30.5	659	
136	30	731	
181	28	1030	
0	43	0	95°C
10	42.5	51	
93	40	314	
160	38	537	
181	37	653	
0	40	0	85°C
34	37	339	
41	365	398	
93	355	519	
136	35	580	
160	345	643	
181	34	706	
0	42	0	75°C
4	41	211	
41	39	321	
160	37	434	

Table IV: Fading data for Durenol Violet 2R on nylon

Exposure (Hrs)	Optical Density (O.D.) x 10^2	Log $(\frac{O.D_o}{O.D_t})$ x 10^4
Temp. 63°C; exposed to light over water		
0	73	0
4	70	182
11	68	308
35	66	438
56	64	571
Temp. 63°C; exposed to light in dry conditions		
0	73	0
15	72	60
31	70	182
56	65	504
102	58	999
113	56	1151

Table IV: Continued

Exposure (Hrs)	Optical Density (O.D.) x 10^2	Log $(\frac{O.D_o}{O.D_t})$ x 10^4
Temp. 100°C; exposed to light over water		
0	68	0
3	64	263
6	55	843
9	53	1082
17	39	2414
26	26	4175
Temp. 100°C; exposed to light in dry conditions		
0	72	0
3	68	248
6	55	1169
11	47	1892
13	42	2341
19	27.5	4180
26	20.5	5455
42	15	5812
50	14.5	6959
66	11	8159

Table V: Fading data for Duranol Fast Yellow G on polyester

Exposure (Hrs)	Optical Density (O.D.) x 10^2	Log $(\frac{O.Do}{O.Dt})$ x 10^4	Temp.
0	40.5	0	
3	33	890	
6	33	890	
12	27.5	1682	
18	24	2273	97°C
35	19.5	3175	
58	18	3522	
81	18	3522	
0	47	0	
3	39	810	
6	38.5	866	
12	33	1536	
18	30.5	1878	82°C
35	26.5	2511	
58	26	2742	
81	25	2742	
0	44	0	
3	39	524	
6	38	637	
12	34	1120	
18	30.5	1592	73°C
35	25.5	2370	
58	24	2633	
81	24	2633	

Table V: Continued

Exposure (Hrs)	Optical Density (O.D.) x 10^2	Log $(\frac{O.Do}{O.Dt})$ x 10^4	Temp.
0	38	0	
3	34.5	420	
6	34	483	
12	30.5	955	69°C
18	25.5	1733	
35	20.5	2680	
58	17.5	3368	
81	17.5	3368	
0	50	269	
3	47	362	
6	46	706	
12	42.5	1135	62°C
18	38.5	1805	
35	33	1939	
58	32	2076	

Table VI: Fading data for Dispersol Fast Orange A on polyester

Exposure (Hrs)	Optical Density (O.D.) x 10^2	Log $(\frac{O.D_0}{O.D_t})$ x 10^4
Temp. 100°C; exposed to light over water		
0	64	0
3	60.5	242
8	52.5	860
10	52	902
14	47.5	1295
17	45	1530
29	37.5	2322
44	23.5	4351
Temp. 100°C; exposed to light in dry conditions		
0	65	0
3	59	420
6	54	805
11	46	1501
13	43.5	1744
19	36	2566
26	30.5	3286
42	19	5341
50	17	5825
66	11.5	7522

Table VI: Continued

Exposure (Hrs)	Optical Density (O.D.) x 10^2	$\text{Log}(\frac{O.Do}{O.Dt})$ x 10^4
Temp. 63°C; exposed to light over water		
0	65	0
4	60	347
11	55	725
20	51	1053
36	44	1694
41	40	2108
56	35	2688
Temp. 63°C; exposed to light in dry conditions		
0	62.5	0
2	59	250
8	55	555
15	50.5	926
31	43	1624
38	39	2048
55	33.5	2709
102	20	4969

Table VII: Fading data for serisol Brilliant Red X-3B on polyester

Exposure (Hrs)	Optical Density (O.D.) x 10^2	$\text{Log}(\frac{O.D_0}{O.D_t})$ x 10^4	Temp.
0	47.5	0	
3	43	440	
10	38	960	
22	34	1240	
29	34	1240	
46	30	2000	97°C
67	27	2460	
90	24	3000	
0	44	0	
22	37	740	
29	35	1003	
46	34	1120	82°C
90	29	1605	
0	51	0	
29	45	640	
46	43	720	
67	39	1123	73°C
90	37	1360	

Contd.

Table VII: Fading data for soricol Brilliant Red X_2B on polyester

Exposure (Hrs)	Optical Density (O.D.) x 10^2	Log $(\frac{O.D_0}{O.D_t})$ x 10^4	Temp.
0	50	0	69^0C
46	43	646	
67	38	1301	
90	36	1404	
0	43	0	62^0C
22	41	212	
46	39	439	
67	36	769	

Table VIII: Fading data for Disperasol Fast Yellow A on polyester

Exposure (Hrs)	Optical Density (O.D.) x 10^2	Log $(\frac{O.D_0}{O.D_t})$ x 10^4	Temp.
0	97	0	
3	93	183	
8	87	473	
15	79	892	
30	63	1875	102°C
59	43	3535	
89	27	5554	
0	96	0	
3	93	138	
8	85	529	
15	80	792	
30	64	1761	96°C
59	43.5	3438	
89	28.5	5275	
0	97	0	
3	93	183	
8	87	423	
15	83	677	90°C
30	68	1543	
59	48.5	3011	
89	31.5	4840	

Table VIII: Continued

Exposure (Hrs)	Optical Density (O.D.) x 10^2	Log $(\frac{O.D_o}{O.D_t})$ x 10^4	Temp.
0	96	0	
3	92	185	
8	89	329	
15	85	529	74°C
30	74	1131	
59	61	1970	
89	46.5	3148	
0	96	0	
3	93	139	
8	90	281	
15	86	478	67°C
30	77	958	
59	65	1694	
89	50	2833	

Table IX: Values obtained of activation energy in fading experiment

Dye	Substrate	Activation Energy
Celliton Fast Pink RP	Polyester	5.42 k.cal/mole.
Dispersol. ~~Dispersol~~ Fast Yellow G	Polyester	3.157 k.cal/mole.
Dispersol Fast Yellow A	Polyester	6.075 k.cal/mole.
Serisol Brilliant Red X_3B	Polyester	4.089 k.cal/mole.
Serisol Brilliant Red X_3B	nylon	15.9 k.cal/mole.
Serisol Brilliant Blue BG	nylon	12.44 k.cal/mole.
Dispersol Fast Yellow G	nylon	18.25 k.cal/mole.

Table X: Quantum Efficiency

Dye	Substrate	Time of Exposure (Hrs)	Quantum Efficiency with Filter			
			Red	Blue	Green	Yellow
Durazol. ~~Duracol~~ Rubine B	Cellophane	156	-	-	2.09×10^{-10}	3.82×10^{-10}
Chlorazol Sky Blue FF	Cellophane	138	-	-	0.1724×10^{-7}	5.08×10^{-8}
Calcodur Yellow RL	Cellophane	138	-	4.577×10^{-5}	-	3.72×10^{-6}
Dispersol Fast Yellow G	nylon	137	-	4.125×10^{-8}	-	6.7×10^{-9}
Dispersol Fast Orange A	nylon	138	-	3.81×10^{-7}	-	4.69×10^{-8}
Methylene Blue BP	Cellophane	176	-	-	2.369×10^{-7}	6.01×10^{-8}

TABLE XI Direct dyes

C.I. No.	Molecular Weight	x/y	x/y Mol. Wt. x 10^3	Light fastness
22250	526	3.1	5.89	4
23640	554	2.94	5.3	5
14140	622	3.5	5.65	4
24895	680	3.3	4.85	4
18780	660	3.0	4.55	2
25220	634	2.86	4.51	4.5
18855	762	3.05	3.95	2.5
22410	554	2.77	5.01	3
22010	561	2.83	5.02	1.5
25300	584	3.44	5.9	4.5
29020	1054	4.3	4.07	6
23660	582	2.77	4.77	5
29035	612	3.05	4.97	4
26280	751	3.33	4.42	3
22920	716	2.63	3.68	3
23365	618	2.8	4.52	1
23375	618	2.7	4.35	1
23380	632	2.7	4.27	2
22130	611	2.94	4.81	1
23370	682	2.7	3.96	1.5
23605	703	2.34	3.3	3
19160	681	2.75	4.05	2
20215	567	2.55	4.5	2
22135	557	2.95	5.3	1.5

Contd.

C.I. No.	Molecular Weight	x/y	x/y Mol. Wt. x 10^3	Light fastness
29155	822	3.44	4.17	2
23665	684	3.1	4.55	3
23655	670	3.1	4.62	3
22385	771	2.9	3.66	4
22310	627	2.27	3.62	3
23500	700	3.1	3.93	1
15080	611	2.2	3.6	2
24100	756	2.95	3.88	1
28105	661.5	3.06	4.62	4
22145	697	3.1	4.45	2
22155	712	2.45	3.44	2.5
29170	852	3.44	3.58	3
27680	637	2.88	4.52	2
22150	697	2.9	4.15	1.5
22280	713	2.13	2.67	1.5
15075	629	2.4	3.82	2
23560	723	2.52	3.47	1
23565	723	2.3	3.17	1
29160	813	3.66	4.48	3
29185	902	3.15	4.49	2.5
22120	696	3.1	4.45	1
22306	627	3.05	4.79	3
22240	676	2.57	3.8	2
23630	704	2.8	3.98	2
14780	567	2.5	4.4	2

Contd.

C.I. No.	Molecular Weight	x/y	x/y Mol. Wt. x 10^3	Light fastness
14985	567	2.25	3.96	3
31525	623	2.9	4.62	2
14990	581	2.25	3.87	2
22290	628	3.0	4.77	3
22405	663	3.05	4.51	2
22420	683	3.28	4.77	4
23040	765	3.1	4.05	1
17875	571	2.45	4.29	3
17870	555	2.65	4.81	3.5
23505	724	2.4	3.31	1.5
23515	589	2.95	5.01	1.5
14785	700	3.22	4.65	2.0
16081	700	2.6	3.71	1.5
28110	511	3.06	5.97	5
28160	675	3.47	5.15	4.5
28180	703	3.47	4.91	5.0
22360	669	2.9	4.35	4.0
28170	689	3.47	5.05	5.0
28165	723.5	3.47	4.77	4.5
28370	830	3.42	4.12	5.5
22570	728	2.52	3.46	3
22555	728	2.45	3.36	3
27660	635	1.83	2.88	3
18100	652	1.92	2.93	2
22550	728	3.1	2.93	2

Contd.

C.I. No.	Molecular Weight	x/y	x/y Mol. Wt. x 10^3	Light fastness
24080	647	2.52	4.12	1
23520	725	3.1	3.9	1
23685	726	3.1	4.27	2
24105	757	2.95	4.23	1
22630	888	3.9	3.9	1.5
23680	726	3.1	4.42	3
22450	713	2.4	4.27	1.5
22440	698	3.1	3.35	2
28190	705	3.27	4.45	1
28200	719	3.1	4.65	5
23705	741	3.0	4.32	5
24140	741	2.95	4.05	1
24170	743	2.95	3.98	1
22485	713	2.9	3.82	2
22565	773	2.9	4.05	1
24310	749	2.6	3.49	1
24280	773	2.7	3.5	1
24205	757	3.01	3.96	1.5
22490	816	2.85	3.49	2.5
23810	756	2.95	3.90	2
30280	766	2.75	3.65	1.5
30295	811	2.9	3.58	1.5
30330	851	2.82	3.42	1.5
30315	878	2.9	3.3	3
30310	878	2.8	3.19	2
30285	800.5	2.75	3.44	2

C.I. No.	Molecular Weight	x/y	x/y Mol. Wt. x 10^3	Light fastness
27540	716	2.0	2.79	3
30290	881	2.85	3.41	4.5
30305	820	2.9	3.54	2
31775	694	2.7	3.06	3
30045	627	3.15	3.8	1
30110	682	3.0	4.31	1
22311	682	2.8	4.45	3
30140	743	3.3	4.85	3
30135	682	3.3	4.85	3
30035	743	2.95	3.97	2
30100	778.5	2.8	3.6	2
30155	732	3.15	4.3	3
31725	867	2.15	2.48	4
34015	747	2.9	3.88	3
22040	575	3.0	5.22	3
31705	746	2.85	3.82	1
22340	656	2.62	3.99	3
22325	628	2.27	3.62	1
30055	730	3.15	4.31	1
30125	795	2.85	3.59	3
30050	782	3.15	4.02	2
20210	738	3.35	4.55	2
22030	559	2.94	5.26	2
34020	813	2.6	3.22	4.5
31740	782	2.75	3.51	5
30120	708	2.85	4.02	2.5

Contd.

C.I. No.	Molecular Weight	x/y	x/y Mol. Wt. x 10^{3}	Light fastness
30070	694	3.01	4.35	2.5
27710	519	2.1	4.05	3.5
30245	795	2.8	3.52	3
30240	815.5	2.8	3.44	3
27700	528	2.37	4.49	5
30395	898	3.05	3.4	3
31580	849	3.15	3.72	2.5
22580	728	2.75	3.78	3.5
30235	781	2.74	3.51	3
31760	766	3.10	4.04	2
34000	720	2.48	3.45	3
34155	873	2.44	2.78	3
29060	1004	2.65	2.65	6.5
29025	942	2.9	3.08	6
29030	972	2.77	2.85	5
20130	838	3.1	3.50	2
29050	1016	2.3	2.28	5
29165	908	3.72	4.10	2.5
23510	826	2.3	2.79	2
29190	938	3.15	3.36	2
23570	826	2.3	2.79	1
29220	962	3.95	4.11	2.5
22180	814	2.54	3.12	1
22205	814	2.26	2.78	2
23050	970	2.26	2.33	2

Contd.

C.I. No.	Molecular Weight	x/y	x/y Mol. Wt. x 10^3	Light fastness
25375	986	2.16	2.19	3
29215	1012	3.0	2.96	2
23600	928	2.3	2.48	2
22200	814	2.35	2.88	1
29175	936	3.15	3.36	2
25380	990	2.45	2.48	4
29065	1048	2.6	2.56	6
25320	990	2.34	2.36	4.5
34025	871	2.05	2.36	4.5
17880	860	3.82	4.45	5
22445	795	3.22	4.05	1
22480	799	2.75	3.45	1
22460	815	3.1	3.80	2.5
22470	799	2.6	3.68	1
22510	902	2.65	3.32	2
25400	1050	2.45	2.34	5
24410	972	3.16	3.25	1
22590	831	2.9	3.48	1
22610	934	3.05	3.26	1
24155	860	2.3	2.67	2
24340	994	3.0	3.02	3
30350	1105	3.1	2.7	2
23850	960	3.2	3.34	1
22475	814	2.67	3.26	1
23710	843	2.9	3.46	1
23790	962	3.2	3.33	2

C.I. No.	Molecular Weight	x/y	x/y Mol. Wt. x 10^3	Light fastness
31930	1030	2.7	2.62	2
23750	828	2.9	3.5	1
31955	1116	2.95	2.66	3
23690	828	3.05	3.69	2
24145	860	3.1	3.61	2
24150	894	2.9	3.24	2
24270	1031	3.1	3.01	1.5
30390	1021	2.85	2.79	2
30205	1081	2.75	2.55	2
22565	830	3.0	3.61	3
22540	934	3.2	3.42	1.5
30340	1003	3.0	2.92	4
23860	960	3.16	3.29	1.5
31910	1084	2.95	2.72	3
24220	875	2.7	3.08	4
34140	1029	2.3	2.24	5
34145	877	2.0	3.28	5.5
34130	979	2.1	2.10	5
21620	751	2.25	3.0	5
32030	1114	3.05	2.44	4
30380	963	2.9	3.01	2
34270	1093	2.35	2.15	5
30365	883	2.85	3.23	3
30345	979	3.05	3.12	3.5
22620	858	3.2	3.74	2
31925	1013	2.95	2.9	3
31810	950	2.9	2.9	3
34180	1131	1.9	1.72	5

TABLE XII Acid dyes: (Mono, di, tri, tetra and penta - sulphonated).

C.I. No.	Molecular Weight	x/y	x/y Mol. Wt. x 10^3	Light fastness
13000	361	1.9	5.3	4.5
13200	270	1.7	6.3	5
13455	385	1.85	6.4	3
14230	341	2.05	6.0	5.5
14610	341	1.75	5.2	3
14625	377	1.6	4.2	2
14695	355	1.8	5.1	3
14710	357	1.65	4.7	5
14805	342	1.9	5.6	3
15540	372	1.6	4.3	4
15575	341	1.6	4.7	3
15620	377	1.6	4.2	2.5
15625	377	1.8	4.8	2.5
15640	377	1.9	5.0	3
17070	482	1.85	3.8	6
17080	553	1.75	3.2	6
17770	418.5	2.2	5.2	5
18695	357	2.2	6.1	5.5
18820	357	2.2	6.1	5.5
18830	371	2.3	6.2	5
18835	527	2.1	4.0	5.5
18850	527	3.05	5.8	5.0
18950	561.5	2.9	5.2	4.5
18960	425	2.05	4.8	5.5

Contd.

C.I. No.	Molecular Weight	x/y	x/y Mol. Wt. x 10^3	Light fastness
19025	439	2.05	4.7	6
20160	397	2.15	5.4	2.5
26420	457	1.8	3.9	5
26665	457	2.35	5.3	4.5
26900	431	2.4	5.4	4
60730	408	1.75	4.3	5
61530	421	1.5	3.5	4.5
62010	387	1.4	3.6	6
62020	409	1.8	4.4	5
62045	399	1.6	4.0	5
62055	416	1.6	3.8	5.5
62085	421	1.7	4.0	5
62105	480	1.7	3.5	5.5
62125	450	1.9	3.8	6
62130	465	1.9	4.1	5.5
62135	404	1.6	4.0	5.5
62145	465	1.9	3.1	6
62155	569	2.0	3.5	5.5
62160	544	4.2	4.2	5.5
63000	349	3.7	3.7	5
63315	401	3.4	3.4	5.5
68200	445	3.4	3.4	3.4
68215	431	3.5	3.5	3.4
68220	446.5	3.1	3.1	3.1
68500	446	3.5	3.5	3.5
13015	355	1.9	5.3	3

Contd.

C.I. No.	Molecular Weight	x/y	x/y Mol. Wt. x 10^3	Light fastness
14720	580	1.85	3.2	3
14730	456	2.1	4.6	3
14835	456	1.85	4.1	3
14895	463	2.35	5.1	4
14900	434	2.05	4.7	5
14905	436	1.8	4.1	5
14910	456	1.9	4.2	3
14920	456	2.25	4.9	4
14940	450	1.65	3.7	4
14965	436	1.6	3.7	5.5
16045	456	1.75	3.8	3
16050	456	1.55	3.4	4
16100	406	1.45	3.6	4
16130	463	1.7	3.7	3
16140	420	1.45	3.8	1.5
16180	456	1.5	3.3	3
16230	374	1.45	3.9	5
16250	456	1.7	3.7	3
16540	422	1.75	4.1	4
16570	422	1.95	4.6	4.5
16580	437	2.05	4.7	2
16595	451	2.05	4.5	2
16600	479	2.15	4.3	4
16605	450	2.0	4.4	5
16625	479	2.15	4.5	4.5

Contd.

C.I. No.	Molecular Weight	x/y	x/y Mol. Wt. x 10^3	Light fastness
16640	472	1.95	4.1	4
17020	452	1.65	3.6	6
17025	466	1.85	4.0	4.5
17030	436	1.8	4.1	6.5
17035	478	1.6	3.4	6
17045	478	2	4.2	6.5
17165	480	2	4.2	4
17185	481	1.95	4.1	3
17200	421	1.95	4.6	2
17750	463	2.2	4.8	5.5
17925	491	2.1	4.3	6
18050	463	1.7	3.7	5
18055	520	1.9	3.7	4
18065	477	1.75	3.7	4.5
18075	493	1.55	3.1	4
18965	505	2.2	4.4	7
19020	484.5	2.2	4.5	6
19040	534.5	2.35	4.4	4.5
20190	526	2.4	4.6	3
20345	570	2.35	4.6	6
20350	575	2.35	4.1	5.5
20415	523	2.15	4.1	3.5
20440	643	2.35	3.7	3
20460	556	2.3	4.1	6
20470	570	2.3	4	5
20495	540	2.25	4.2	4

Contd.

C.I. No.	Molecular Weight	x/y	x/y Mol. Wt. x 10^3	Light fastness
20500	582	2.3	4	5
22890	612	2.6	4	4
23285	680	3.0	4.4	5
23290	680	2.65	3.9	4
23910	680	2.45	3.6	4
24500	658	2.25	3.4	2
26905	510	2.35	2.4	3.5
27000	510	2.0	4.7	4
27155	510	2.4	4.7	4
27165	538	2.4	4.5	5.5
27190	510	1.9	3.7	4
27200	536	1.95	3.6	4.5
27290	510	2.2	4.3	6
27510	516	2.2	3.8	6.5
61125	529	1.8	3.4	6
61130	782	2.7	3.4	6.5
61560	658	1.03	1.6	5.5
61570	576	1.1	2.0	6
61580	660	1.35	2.1	6
61565	632	1	1.6	6
61590	742	1.2	1.6	6
61595	702	1.25	1.8	6
61170	576	2.5	4.3	6
61800	576	1.75	3.0	6
62005	396	1.3	3.3	5.5
62026	580	1.0	1.7	6

Contd.

C.I. No.	Molecular Weight	x/y	x/y Mol. Wt. x 10^3	Light fastness
62076	486	1.7	3.5	5.5
62095	499	1.7	3.4	5
62110	565	1.7	3.0	6.5
62550	592	1.25	2.1	6
62560	608	1.2	2.0	6.5
62575	698	1.55	2.2	6
63010	428	1.3	3.0	5.5
65000	581	3.0	5.1	6
68205	510	1.45	2.9	6
19120	465	2.1	3.7	6
19140	649	2.45	4.5	4
20480	732	2.75	3.8	5
23000	879	2.2	3.8	3.5
23010	785	1.6	2.5	4
26990	668	2.05	2.0	4
27195	768	1.7	3.1	3.5
27260	732	2.3	2.2	6
27300	654	2.3	3.1	4
27790	534	1.75	3.5	6.5
16255	613	1.5	3.3	4
16290	551	1.9	2.4	4.5
16645	465	1.7	3.6	4.5
17190	672	2.1	3.1	2

TABLE XIII Disperse dyes

C.I. No.	Molecular Weight	x/y	x/y Mol. Wt. x 10^3	Light fastness
10340	259	1.24	4.79	3.5
10345	275	1.3	4.72	4.5
10350	278.5	1.3	4.67	7
11005	242	1.54	5.75	5
11040	300			
11080	318	2.48	7.8	6
11100	369	2.06	5.47	5
11110	320	2.56	7.8	5
11115	354.5	2.5	7.0	6
11118	342	2.47	7.2	4.5
11130	330	2.5	7.5	4.5
11150	364.5	2.5	6.85	5.5
11190	383	2.2	5.75	6
11210	344	2.5	7.25	5.5
11215	378.5	2.33	6.15	5.5
11225	360	2.2	6.1	4.5
11240	270	2.0	7.4	5.0
11250	270	1.77	6.55	5.0
11430	398.5	1.55	3.9	4.0
11435	406	1.9	4.15	4.0
11855	269	2.43	9.0	5.5
12770	265			
12790	311	1.77	5.65	5
12795	311	1.88	6.07	3

Contd.

C.I. No.	Molecular Weight	x/y	x/y Mol. Wt. x 10^3	Light fastness
56060	365	2.38	6.47	6.5
56200	340	1.56	4.57	1
58900	340			
60505	237	1.44	5.08	5
60700	237	1.6	6.75	3.5
60710	223	1.3	5.85	6
60755	269	1.59	5.9	7
61100	238	1.3	5.45	6
61105	252	1.28	5.07	5
61110	314	1.58	5.02	6.5
61140	264	1.32	5.65	6.5
61500	266	1.15	4.3	5
61505	280	1.28	4.5	5
61510	330	1.45	4.55	4
61515	328	1.43	4.35	6
61545	326	1.2	3.68	4.5
62015	252	1.63	6.47	5
62030	283	1.31	4.6	6
62050	363	1.58	4.3	7.5
62065	407	1.55	3.5	7
62500	408	1.18	3.2	6
63305	298	1.33	4.45	6
64500	268	1.3	4.85	3.5
10375	274	1.47	6.35	5
12700	278	1.95	6.2	4

Contd.

C.I. No.	Molecular Weight	x/y	x/y Mol. Wt. x 10^3	Light fastness
26080	352	2.1	5.95	6
62038	295	1.39	5.3	7
61115	344	1.69	4.91	6-5
60715	253	1.41	5.55	5

TABLE XIV Anthraquinone Vat dyes

C.I. No.	Molecular Weight	x/y	x/y Mol. Wt. x 10^3	Light Fastness
58950	377	2.82	7.45	4
59100	332	1.7	5.05	5.5
59300	384	1.25	3.68	7.5
59700	406	1.7	4.20	5.5
59800	456	2.3	5.05	6.5
59825	520	1.86	3.58	7
59835	544	1.77	3.25	7
59850	546	2.53	4.67	6
59820	594	2.32	3.9	6.5
60005	456	2.3	8.05	5.5
60015	516	1.61	2.08	6.5
60705	498	3.06	6.15	6.5
61650	446	1.52	3.4	7
61655	506	1.52	2.98	7
61670	736	2.24	3.50	7
61725	446	2	4.50	6
63355	478	2	4.17	6
63365	538	1.92	3.55	6.5
64015	565	1.39	2.46	7
65400	528	2.2	2.57	5.5
65405	706	3.3	4.67	5
65410	619	2.14	3.47	5.5
65415	814	2.1	2.58	7.5
65420	814	3.3	4.05	5

Contd.

C.I. No.	Molecular Weight	x/y	x/y Mol. Wt. x 10^3	Light fastness
65425	814	3.3	4.10	4.5
65435	456	2.87	5.6	7.5
67820	694	2.85	3.96	8
67895	427.5	1.68	3.94	7.5
67900	497.5	1.68	3.38	7.0
67910	374.5	1.5	3.90	7.5
67915	409	1.57	3.84	6.5
67920	493	1.41	2.86	6.5
68000	375	1.78	5.07	8.0
68400	385.5	1.43	3.72	6
68405	420	1.65	3.94	6
68420	481	1.77	3.68	7
68700	442	2.3	4.6	7
69500	451	2.3	5.1	8
69515	570	2.45	4.3	8
69540	489.5	2.16	4.4	7
69800	442	2.16	5.87	7.5
69815	477	1.63	3.42	7.5
69825	510	1.63	3.19	7.5
69845	473	1.9	4.01	7
69850	541	1.81	3.55	7.5
70600	407	1.75	4.3	5.5
70695	604	2.04	3.38	6
71135	491	3.06	6.2	5
71140	602	3.23	5.4	6
56050	283.5	2.05	7.0	7

Legends for Figs. 1A & 1B

Fig. 1A Close view of tubes fixed around mercury vapour lamp, on inner surface of aluminium shield. Water or calcium chloride were for certain experiments placed at the bottom of the tubes.

Fig. 1B Detailed view of Fig. 1A showing heating units inserted in tubes.

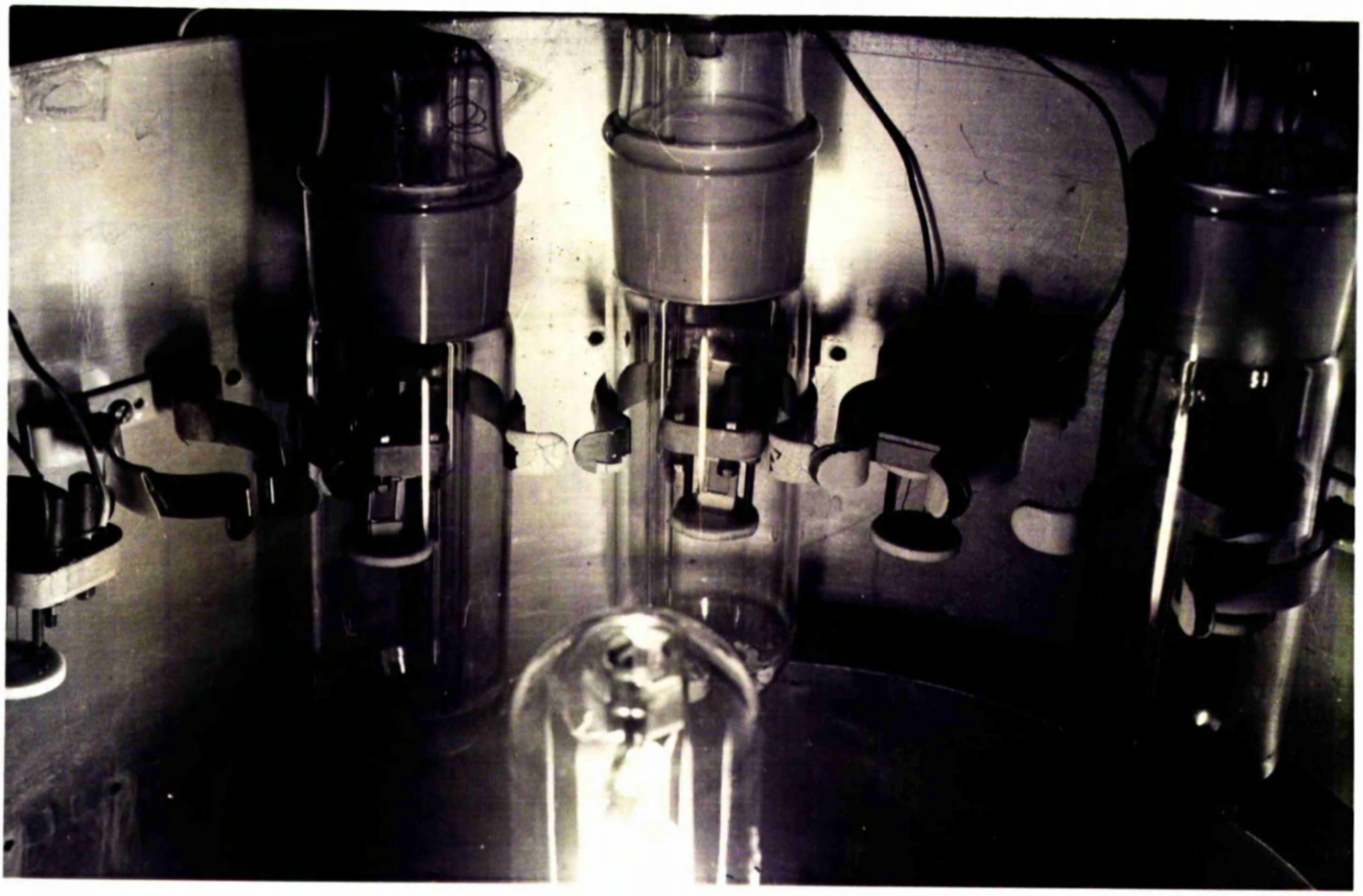


Fig. 1A

Fig. 1B

Fig. 2. Device for dyeing Cellophane film. The film is bound round the lacquered brass wire frame and rotated in the dyebath by the slow-speed (clock) motor.

Fig. 2.

Legend for Fig. 3 — A general view of the fading lamp used as a source of irradiation during this investigation. Jacketted tubes shown in the photograph were not used in this work, but were used by author's colleague.

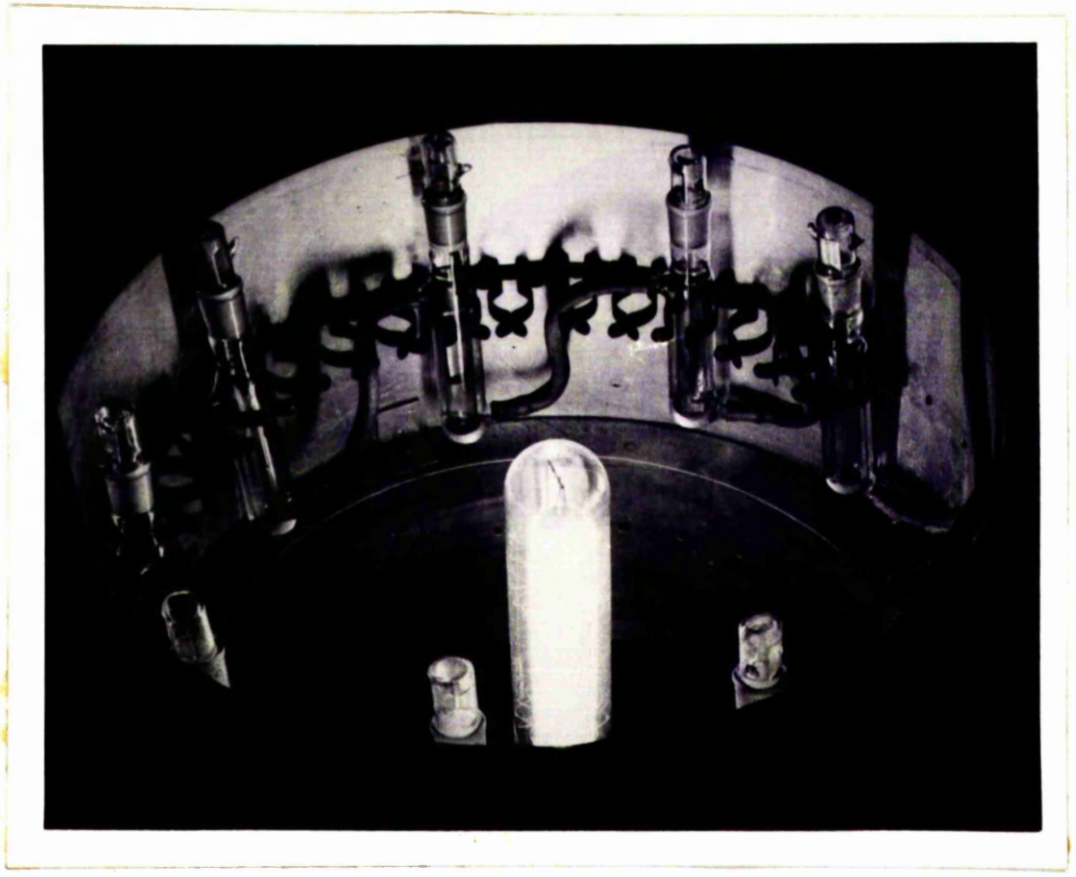


Fig. 3

Legend for Fig. 4 — Absorption curves of dyed films used in quantum efficiency experiment.

A - Durazol Rubine B.

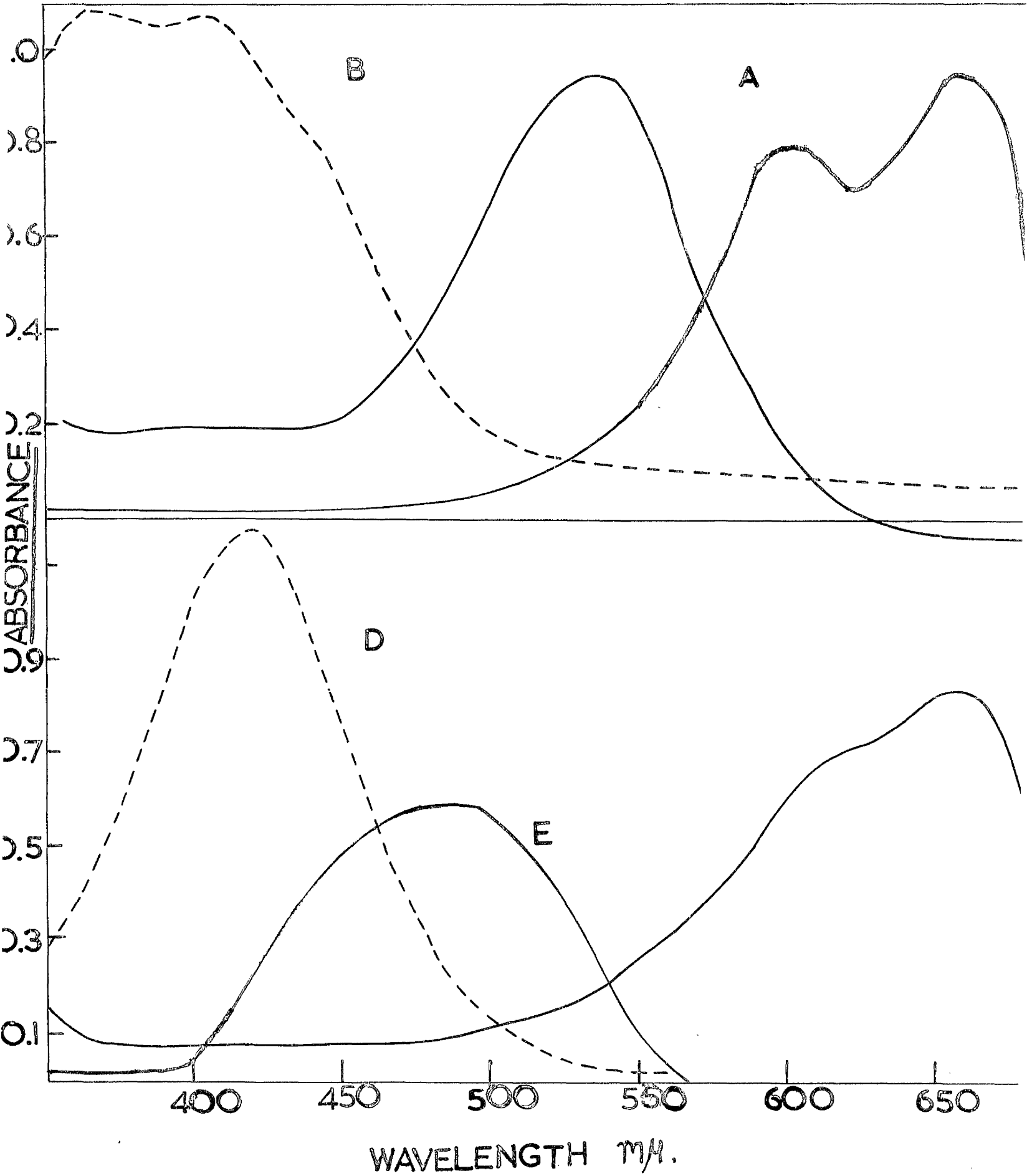
B - Dispersol Fast Yellow G.

C - Chlorazol Sky Blue FF.

D - Calcodur Yellow RL.

E - Dispersol Fast Orange A.

F - Methylene Blue BP.


B
A
D
E
ABSORBANCE
1.0
0.8
0.6
0.4
0.2
0.9
0.7
0.5
0.3
0.1
400
450
500
550
600
650
WAVELENGTH mμ.

Legend for Fig. 5 — Transmission curves of the filters used in quantum efficiency experiment.

(i) Blue filter

(ii) Yellow filter

(iii) Green filter

(iv) Red filter

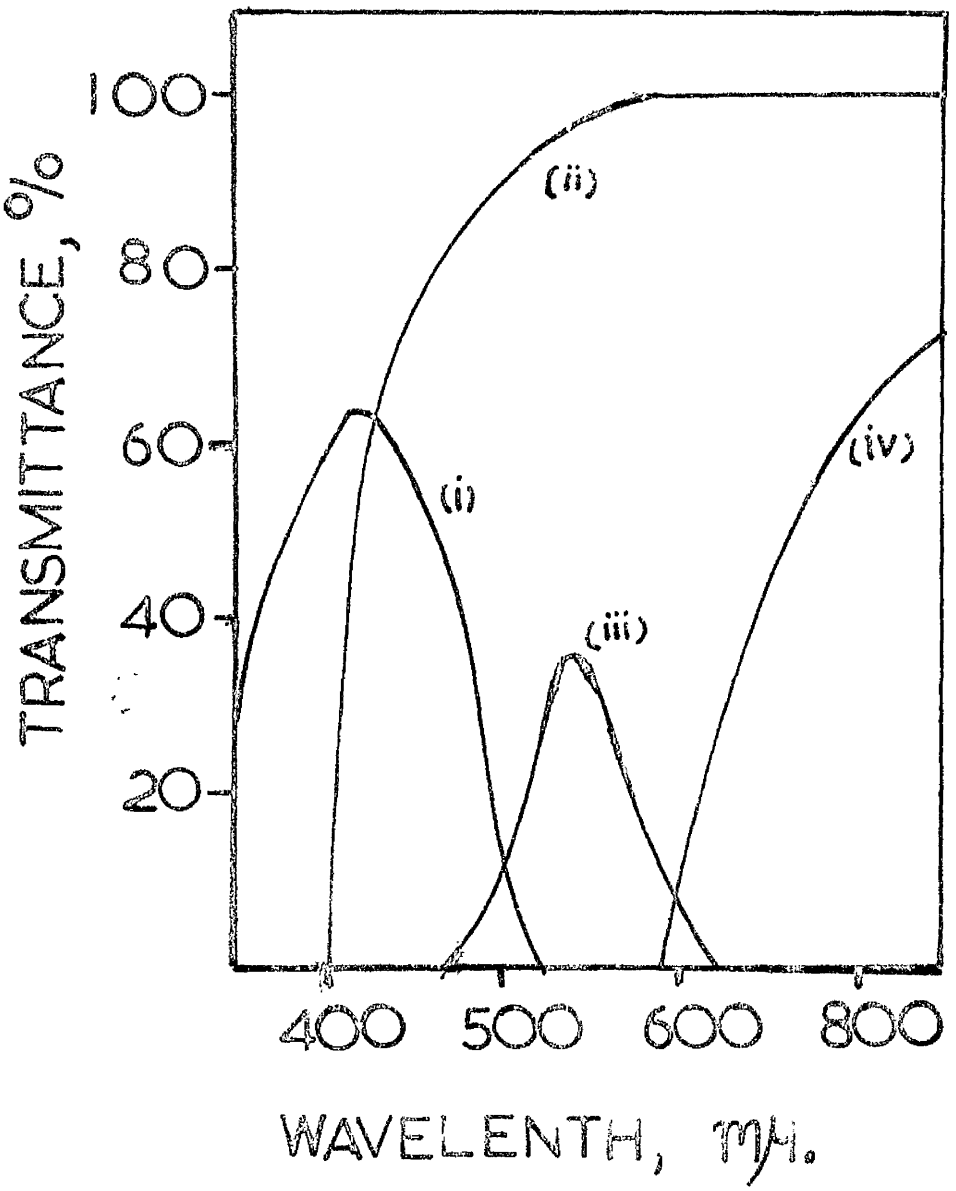

TRANSMITTANCE, %
100
80
60
40
20
(i)
(ii)
(iii)
(iv)
400
500
600
800
WAVELENTH, mμ.

Fig. 5

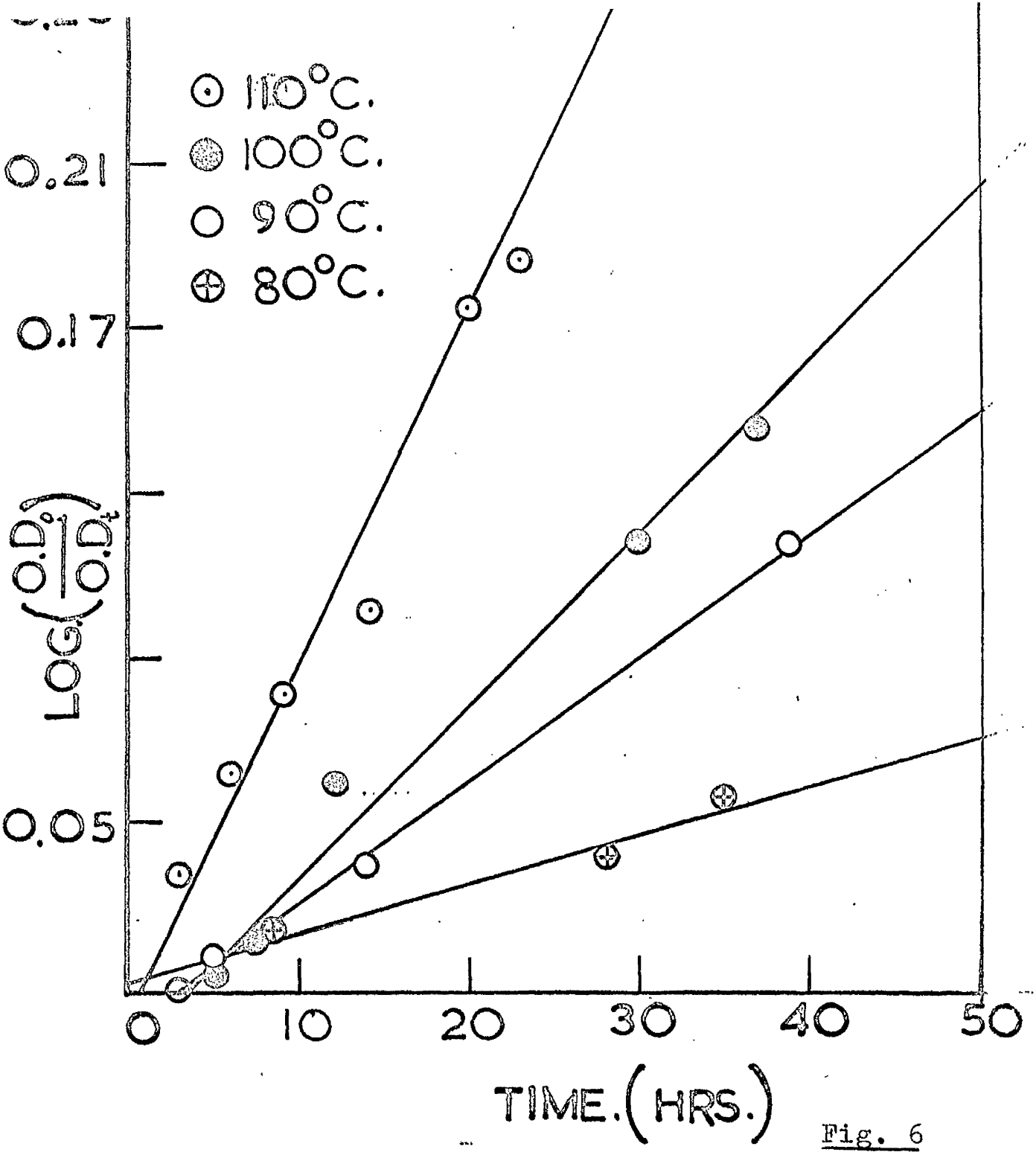


Fig. 6

Legends of Fig. 6 Dispersol Fast Yllow G on nylon

Legend for Fig. 7 Disperesol Fast Yellow G on nylon.

Linear relationship between log k and the reciprocal of the absolute temperature.

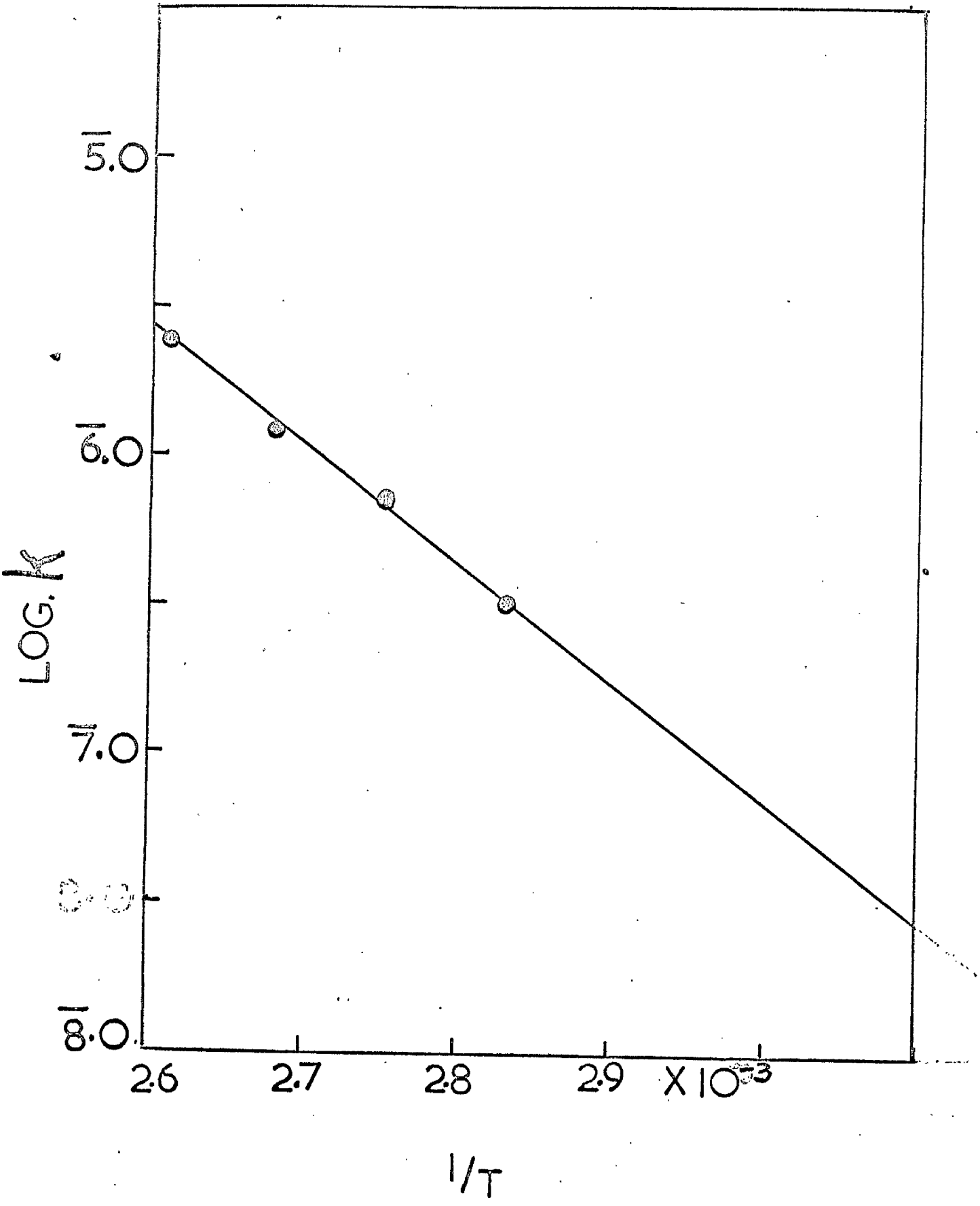


Fig. 7

Legend for Fig. 8 Duranol Fast Yellow G on polyester.

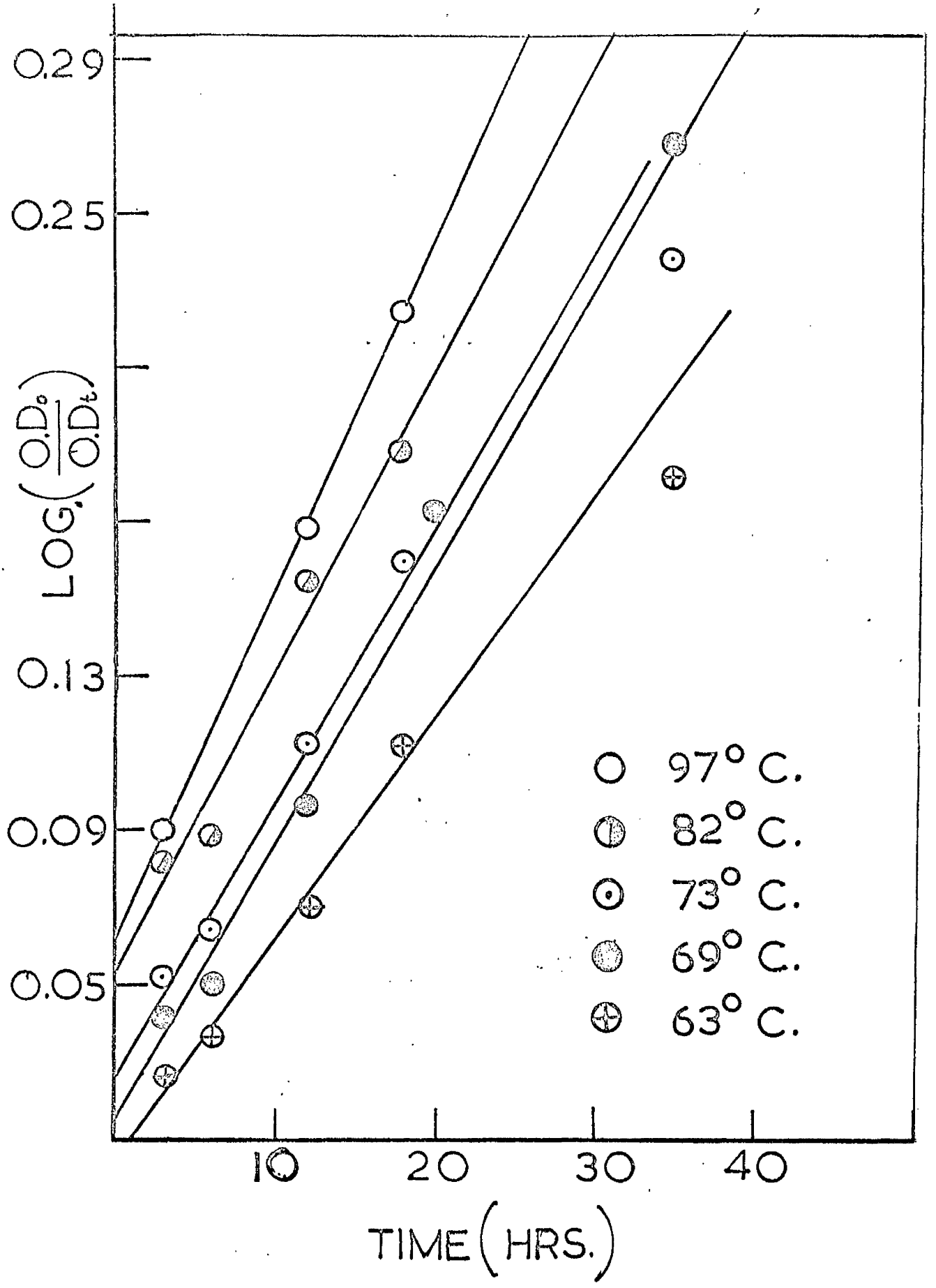

0.29
0.25
0.13
0.09
0.05
LOG.(O.D.°/O.Dt.)
10
20
30
40
TIME (HRS.)
97° C.
82° C.
73° C.
69° C.
63° C.

Fig. 8

Legend for Fig. 9 Duranol Fast Yellow G on polyester.

Linear relationship between log k and the reciprocal of the absolute temperature.

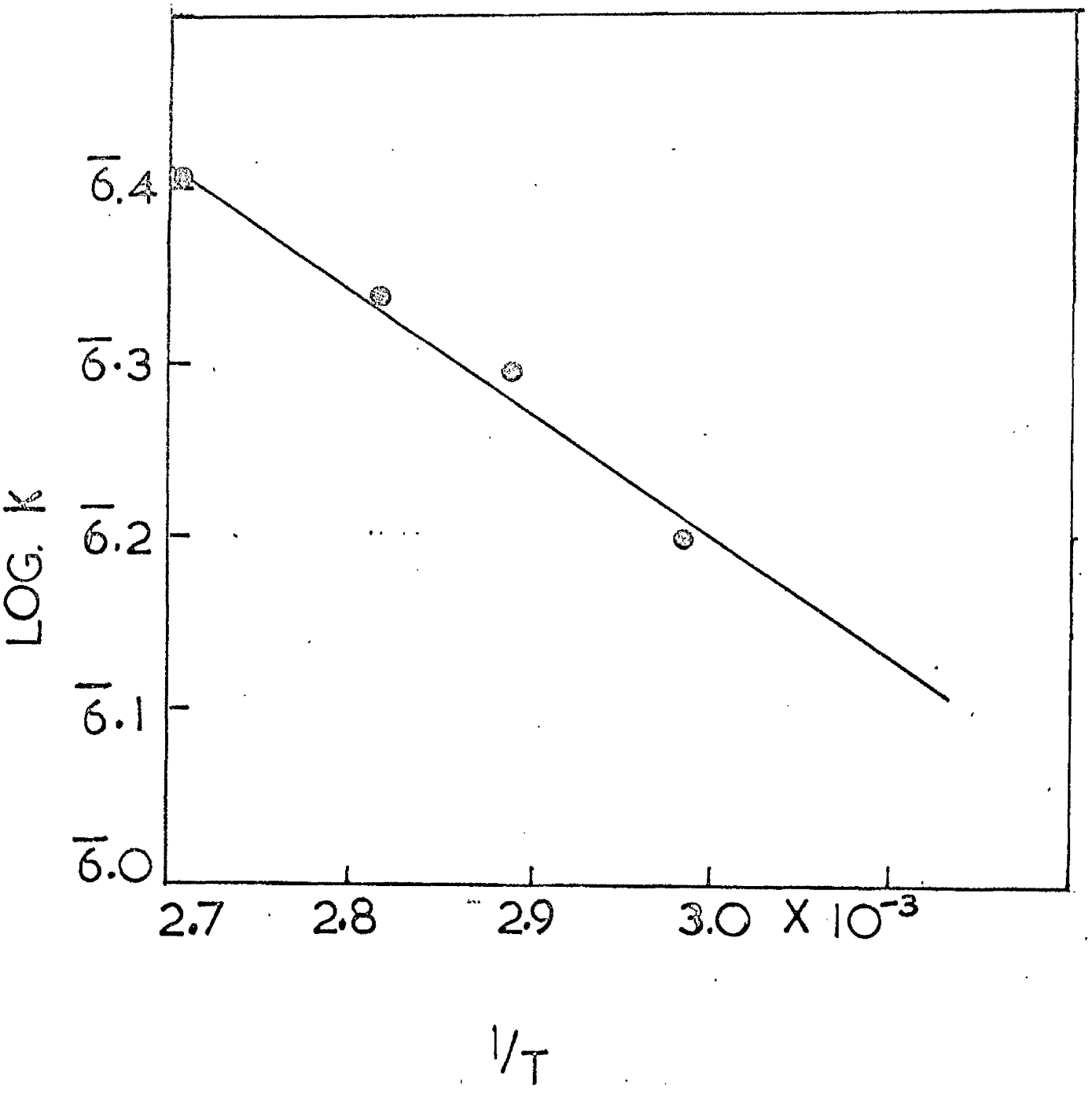


Fig. 9

Legend for Fig. 10 Servinol Brilliant Red X3B on nylon.

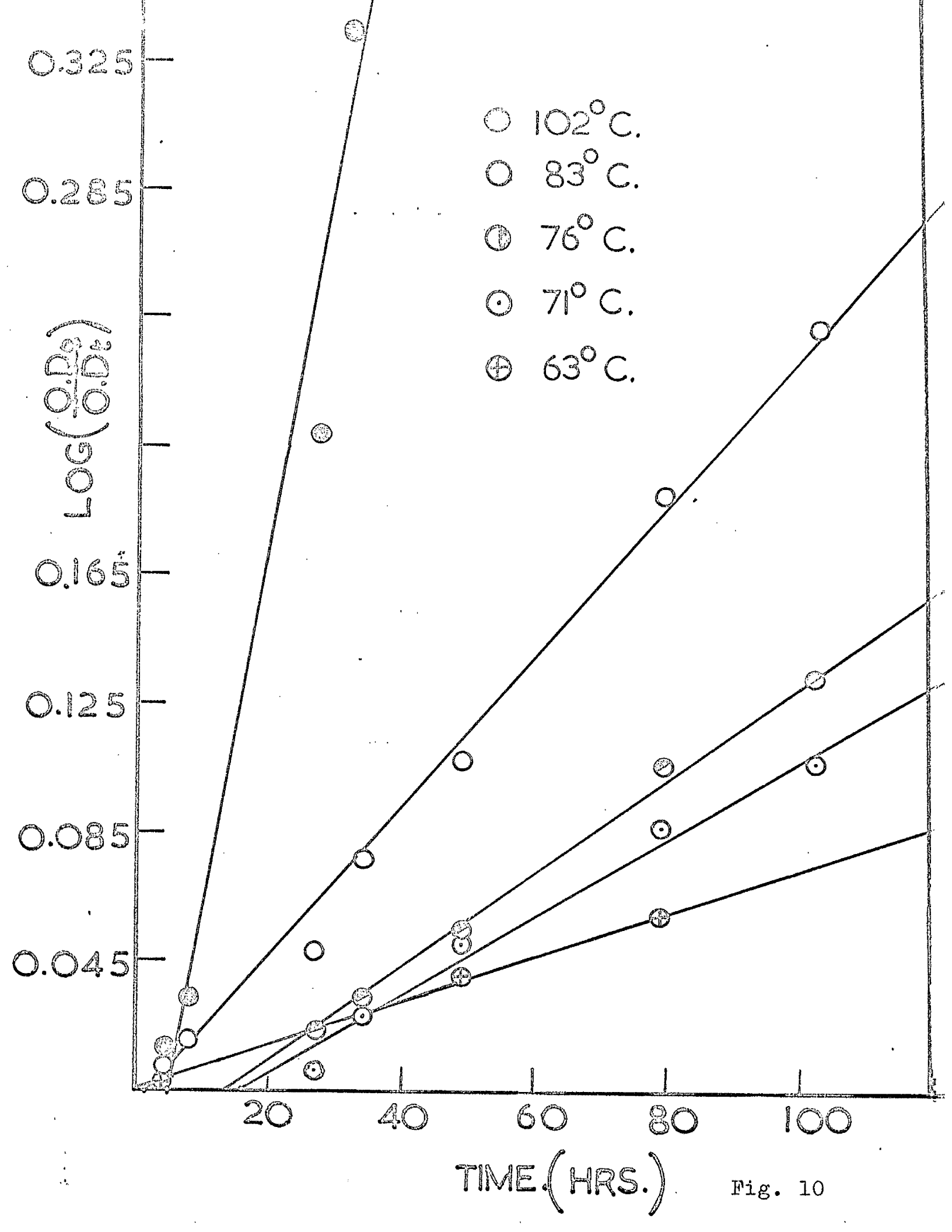

0.325
0.285
0.165
0.125
0.085
0.045
Log (o.p.s.)
102° C.
83° C.
76° C.
71° C.
63° C.
20
40
60
80
100
TIME (HRS.)

Fig. 10

Legend for Fig. 11 Serisol Brilliant Red X3B on nylon.

Linear relationship between log k and the reciprocal of the absolute temperature.

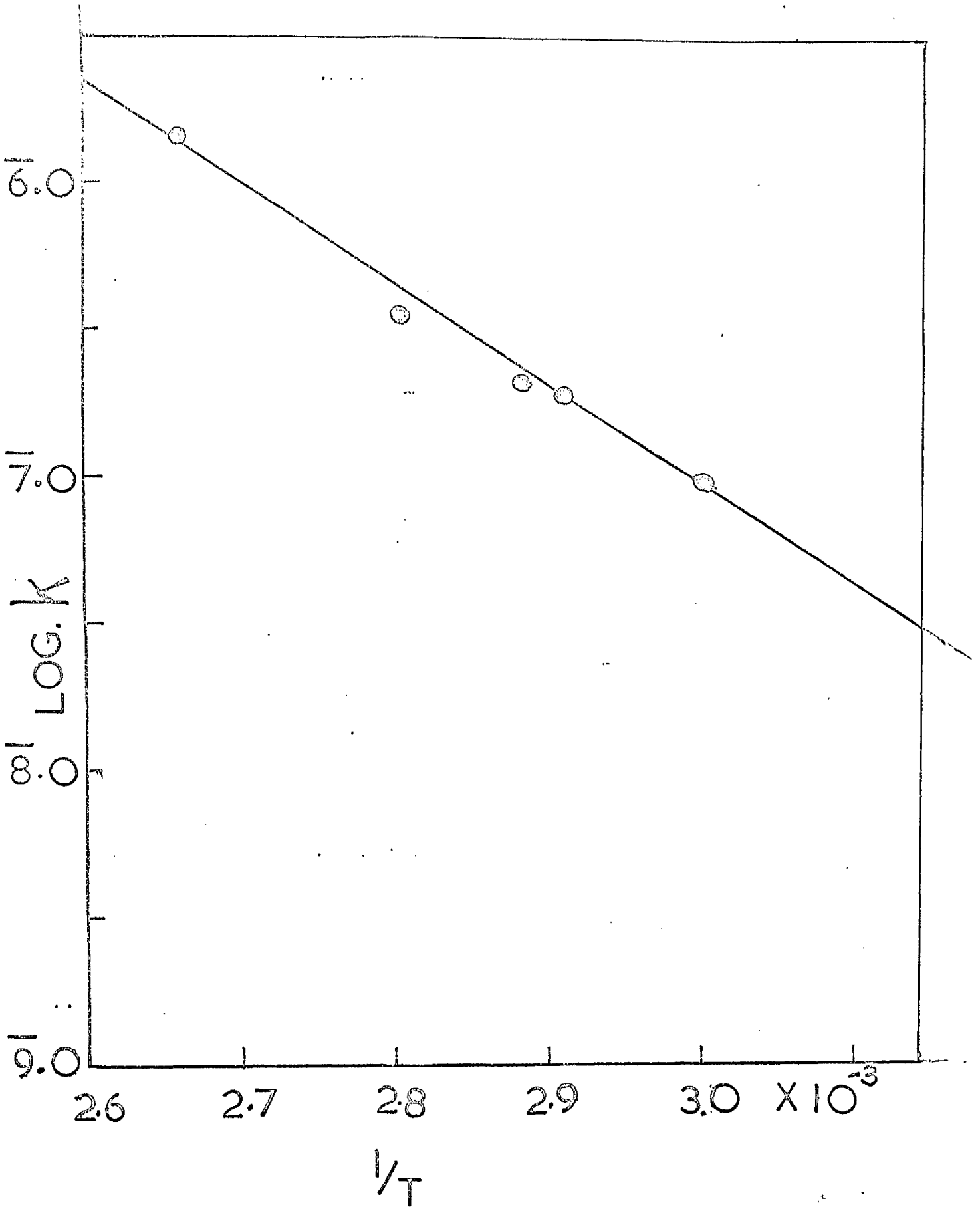


Fig. 11

Legend for Fig. 12 Serisol Brilliant Red X3B on polyester.

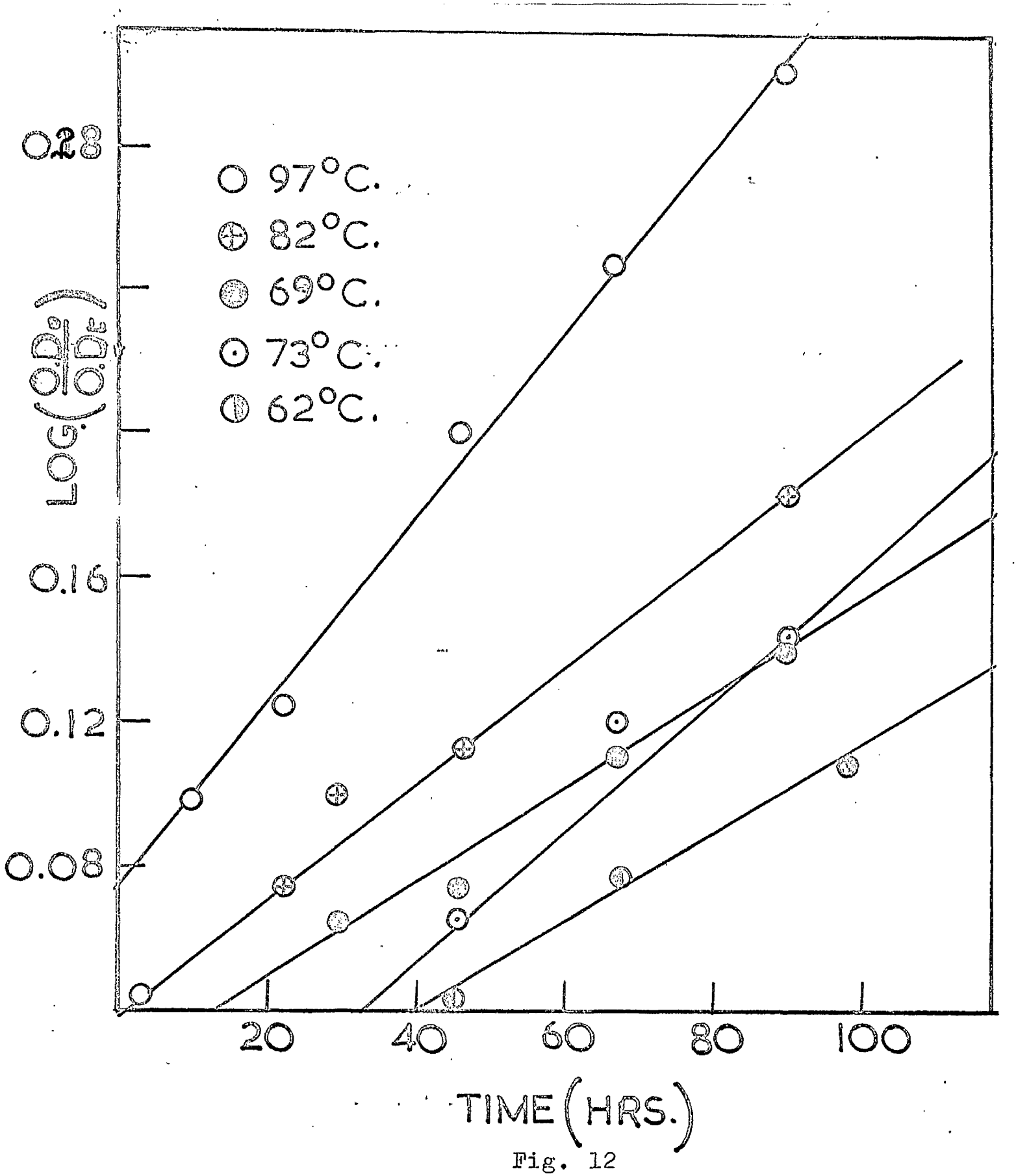

0.28
0.16
0.12
0.08
Log(a/a-x)
97°C.
82°C.
69°C.
73°C.
62°C.
20
40
60
80
100
TIME (HRS.)

Fig. 12

Legend for Fig. 13

Soriasol Brilliant Red X3B on polyester.

Linear relationship between log k and the reciprocal of the absolute temperature.

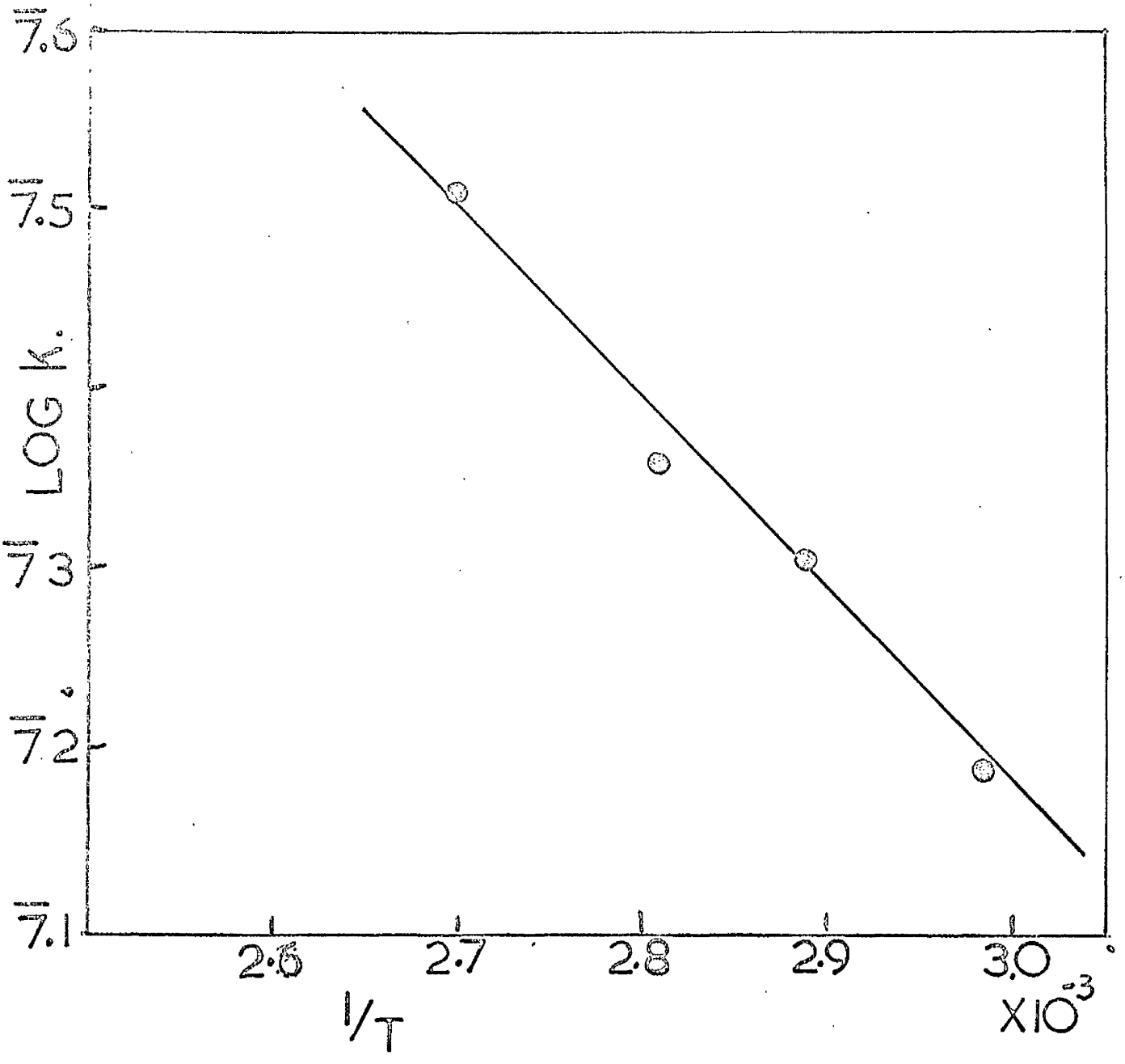


Fig. 13

Legend for Fig. 14. Dispersol Fast Yellow A on polyester.

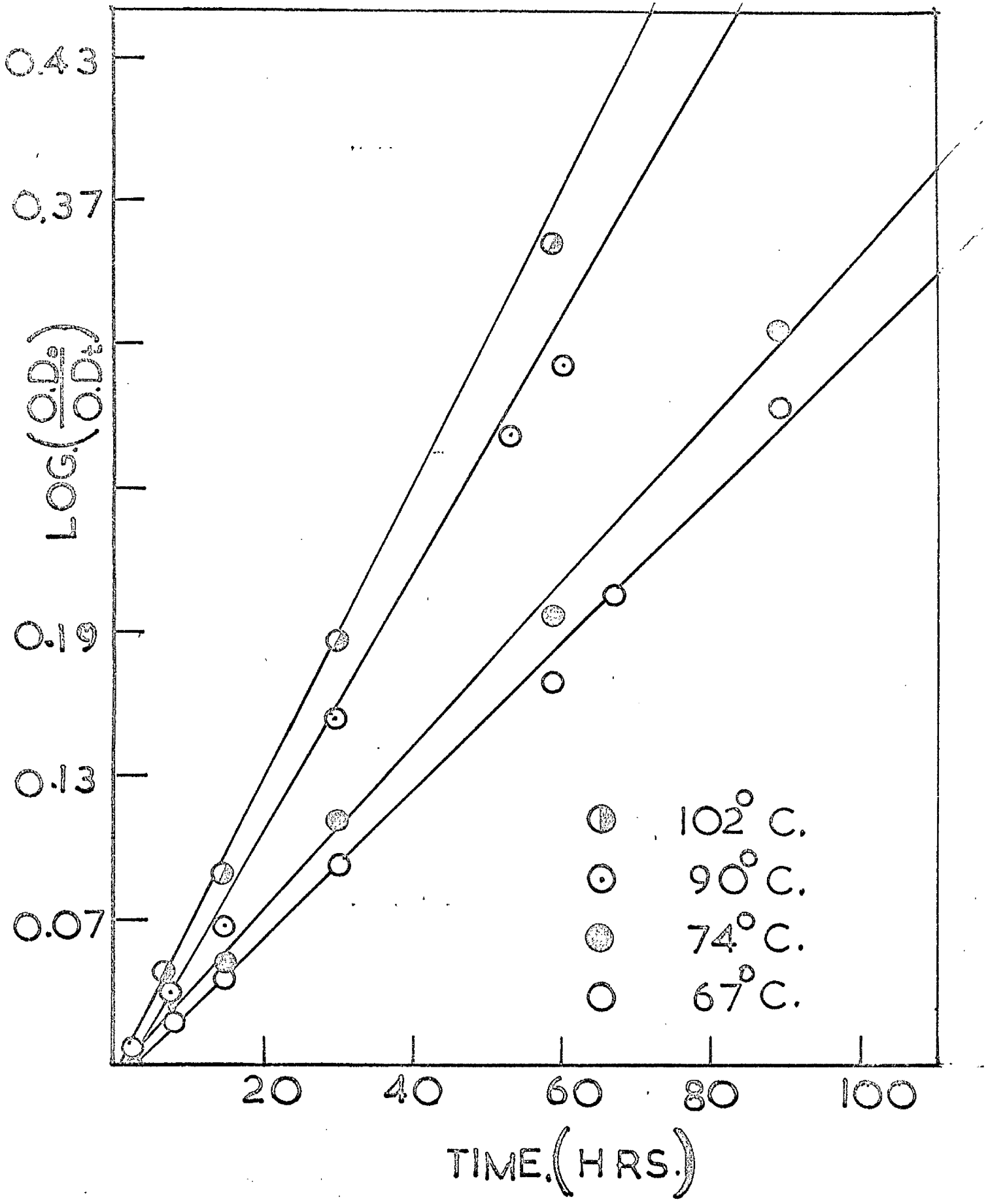

0.43
0.37
0.19
0.13
0.07
LOG.(O.D.₀/O.D.t)
102° C.
90° C.
74° C.
67° C.
20
40
60
80
100
TIME.(HRS.)

Fig. 14

Legend for Fig. 15 Disperasol Fast Yellow A on polyester.

Linear relationship between log k and the reciprocal of the absolute temperature.

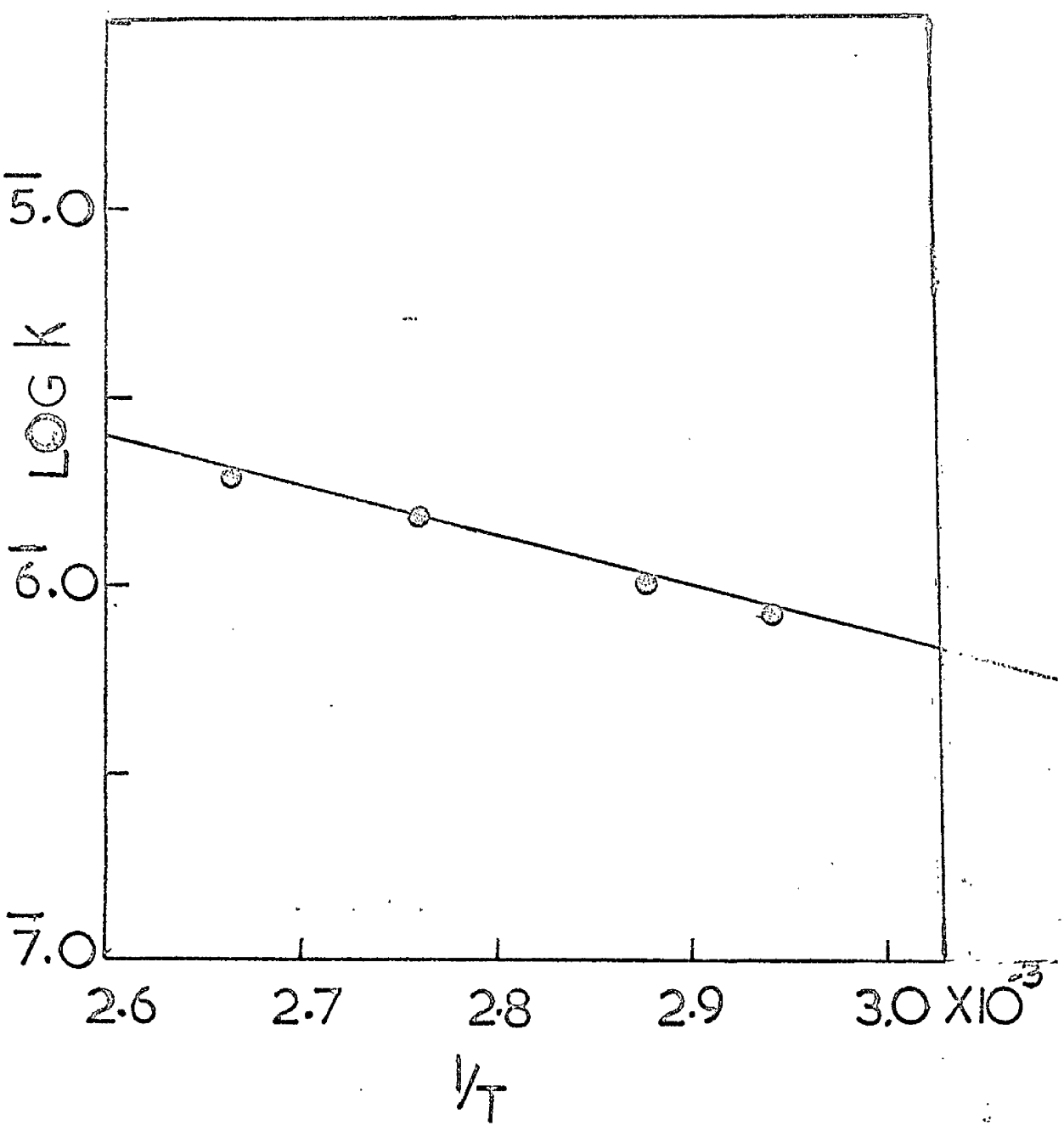


Fig. 15

Legend for Fig. 16 Serisol Brilliant Blue BG on nylon.

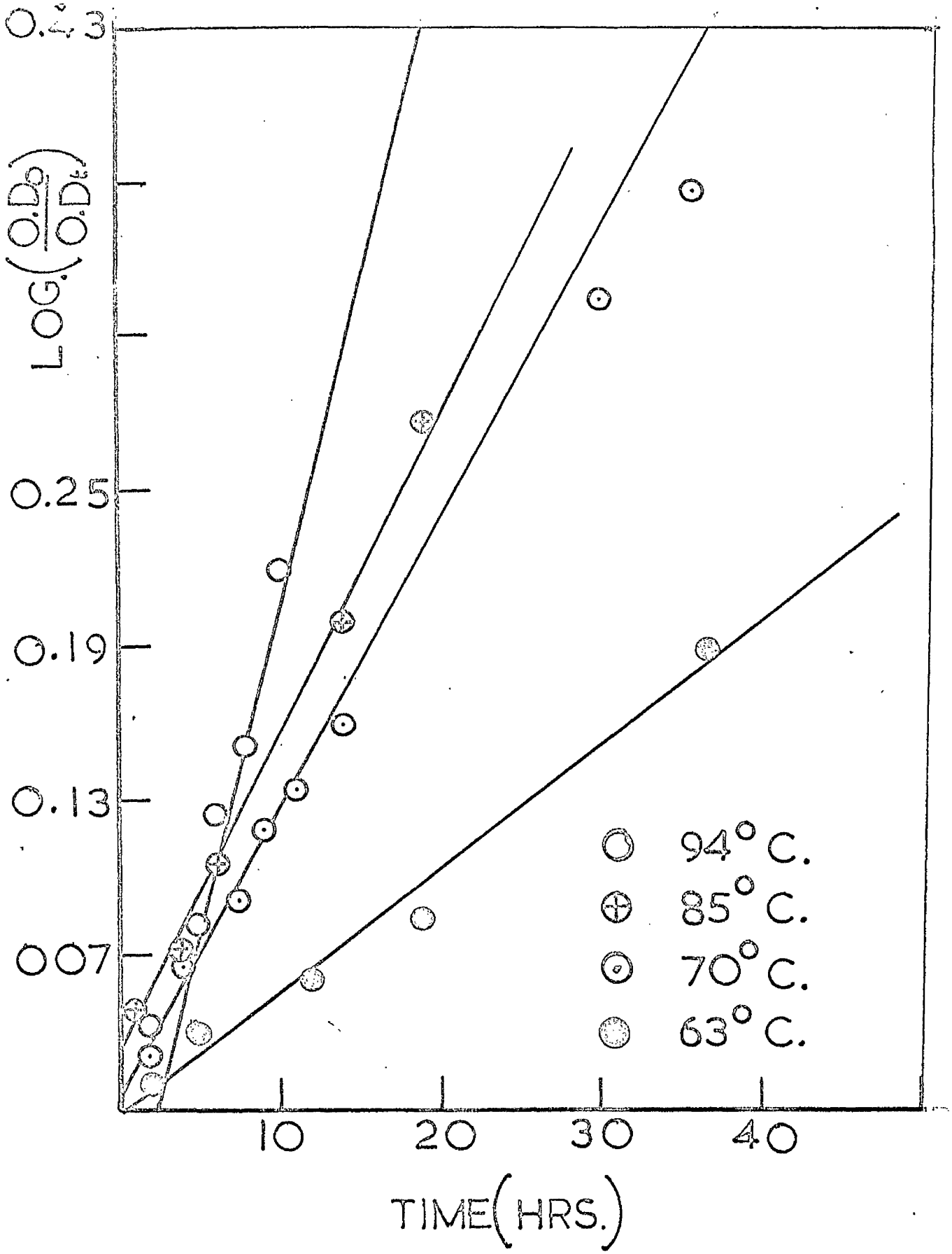

0.43
LOG.(O.D.o/O.Dt.)
0.25
0.19
0.13
007
94° C.
85° C.
70° C.
63° C.
10
20
30
40
TIME(HRS.)

Fig. 16

Legend for Fig. 17 Serisol Brilliant Blue BG on nylon.

Linear relationship between log k and the reciprocal of the absolute temperature.

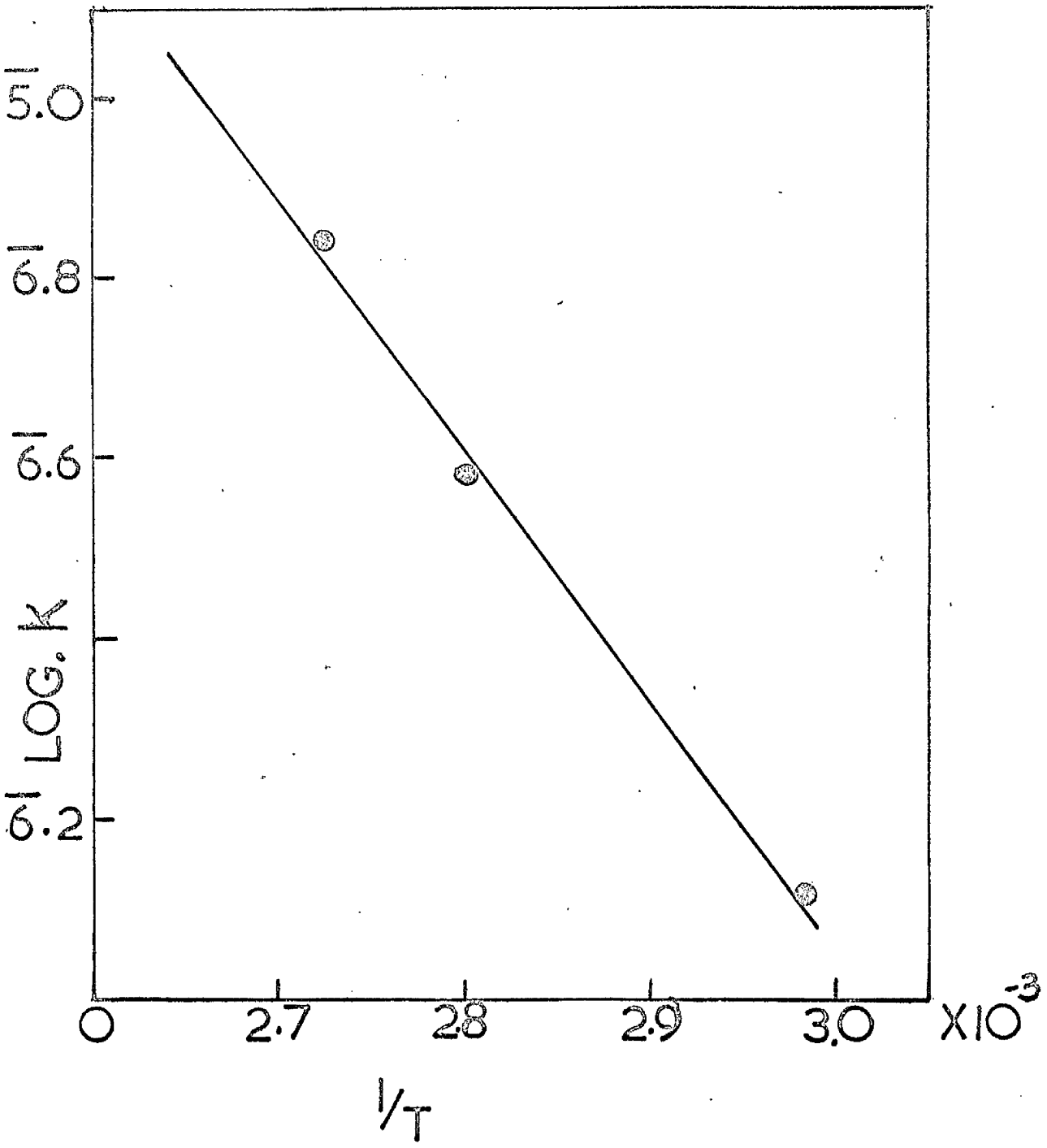


Fig. 17

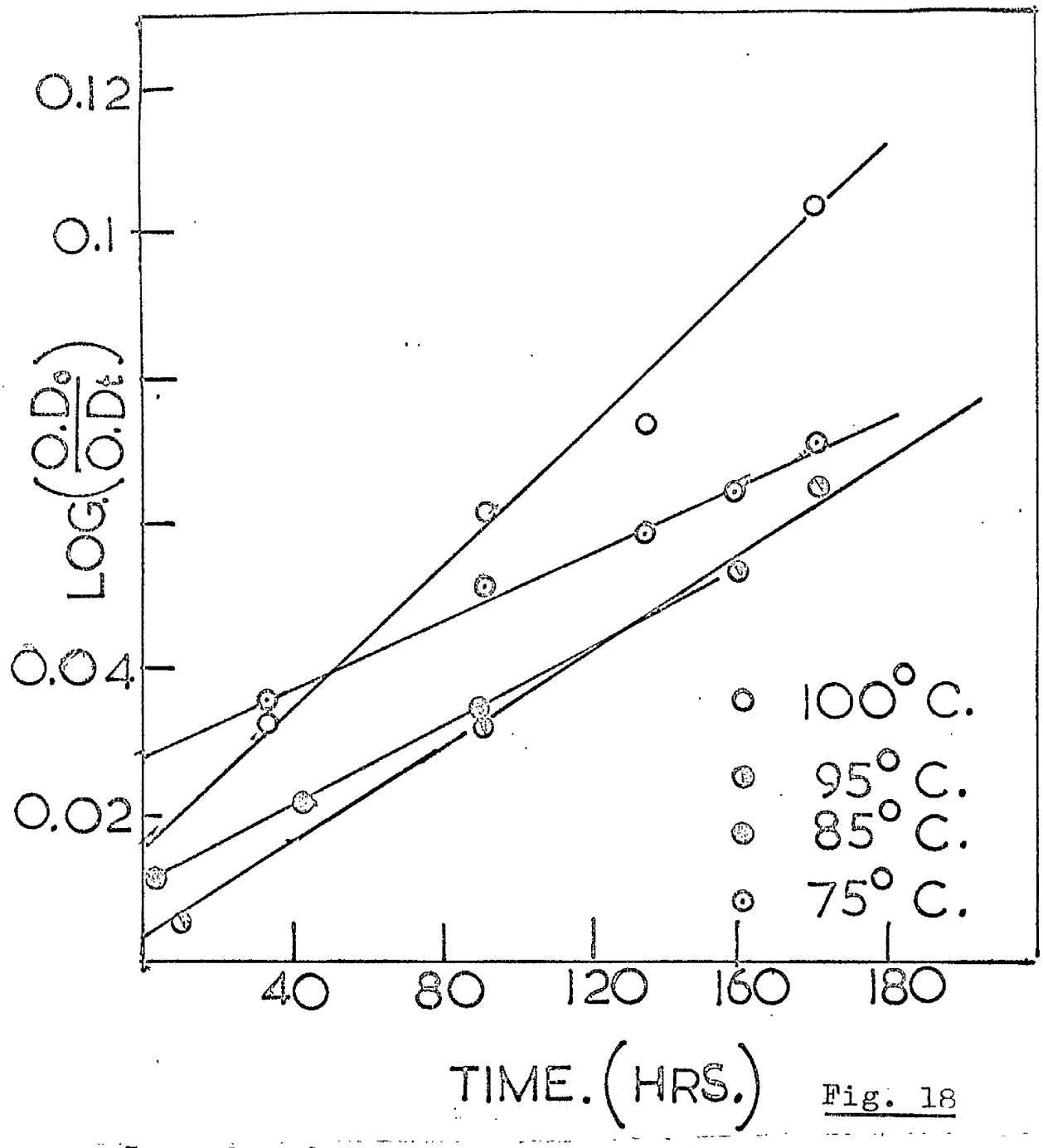


Fig. 18

Legends of Fig. 18 Celliton Fast Pink RF on Polyester.

Legend for Fig. 19 Celliton Fast Pink RF on polyester.

Linear relationship between log k and the reciptrocal of the absolute temperature.

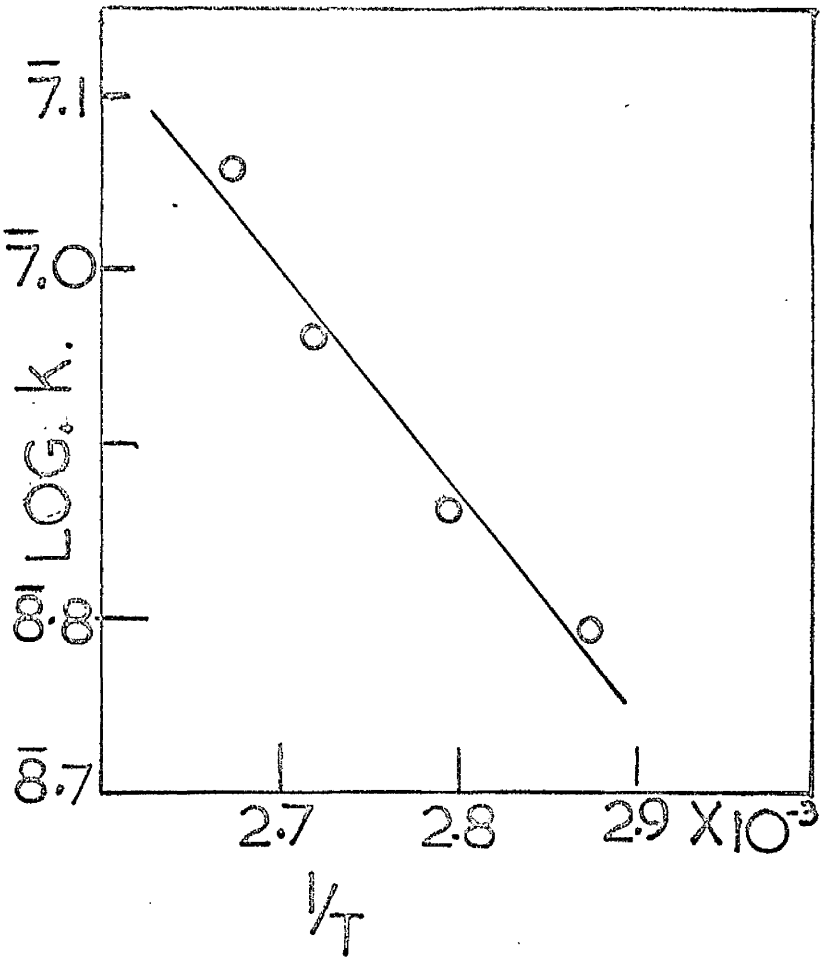


Fig. 19

Legend for Fig. 20 Duranol Brilliant Violet BR on polyester.

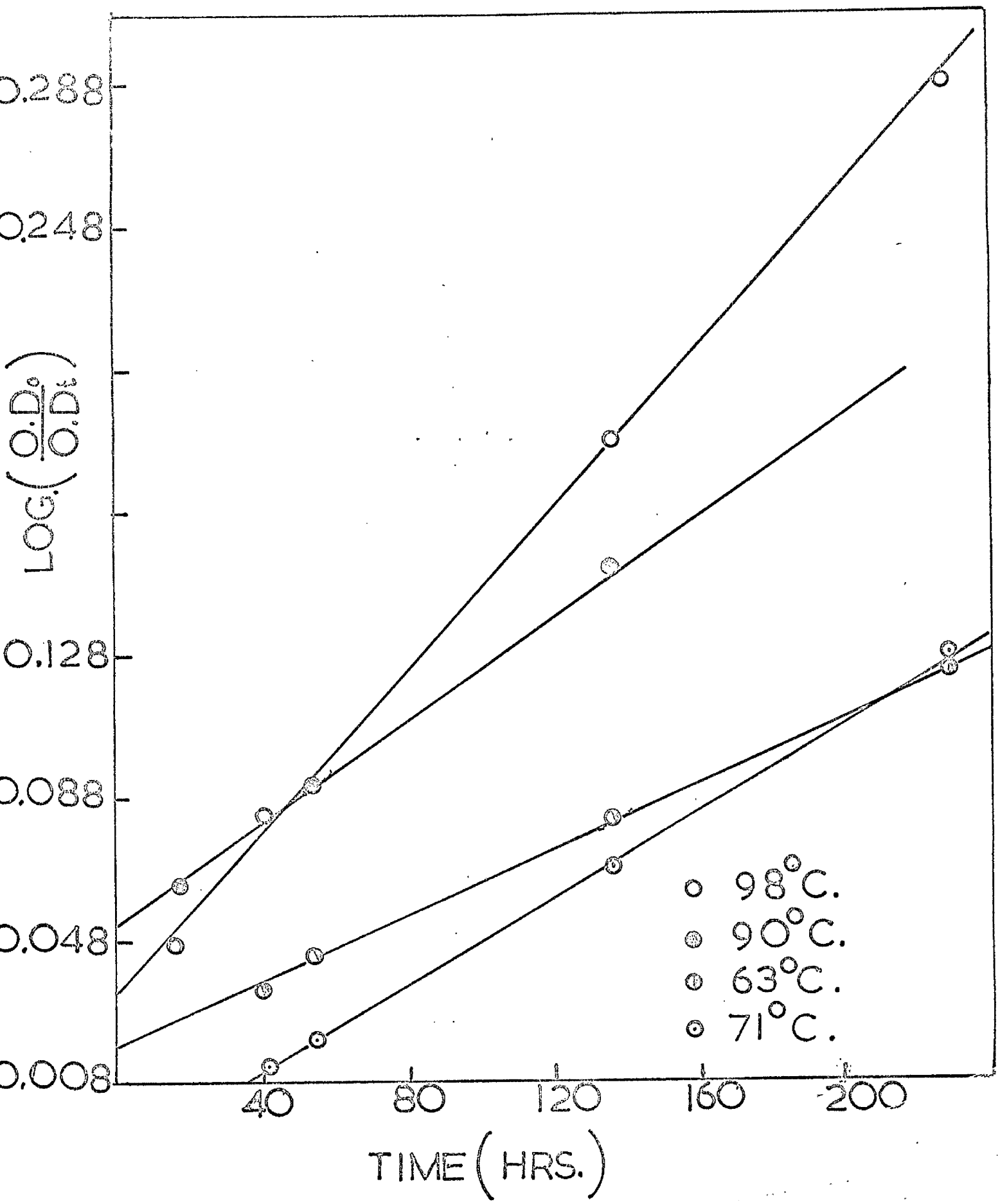

0.288
0.248
0.128
0.088
0.048
0.008
LOG.(O.D.°/O.Dt.)
40
80
120
160
200
TIME (HRS.)
98°C.
90°C.
63°C.
71°C.

Fig. 20

Serisol Brilliant Green 3G on nylon

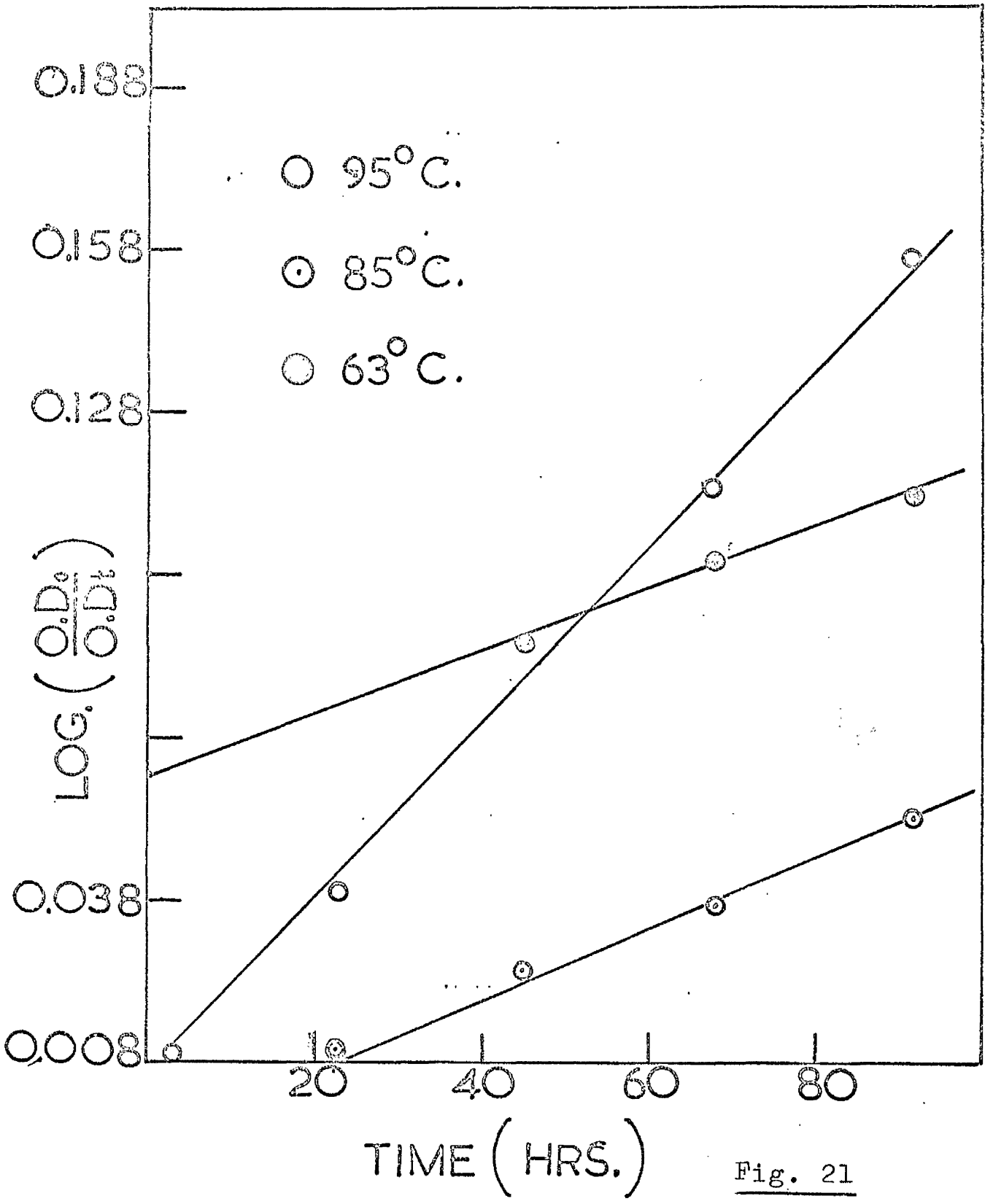


Fig. 21

Legends of Fig. 21 Serisol Brilliant Green 3G on nylon.

Legend for Fig. 22 Duasol Orange 20 on Cellophane

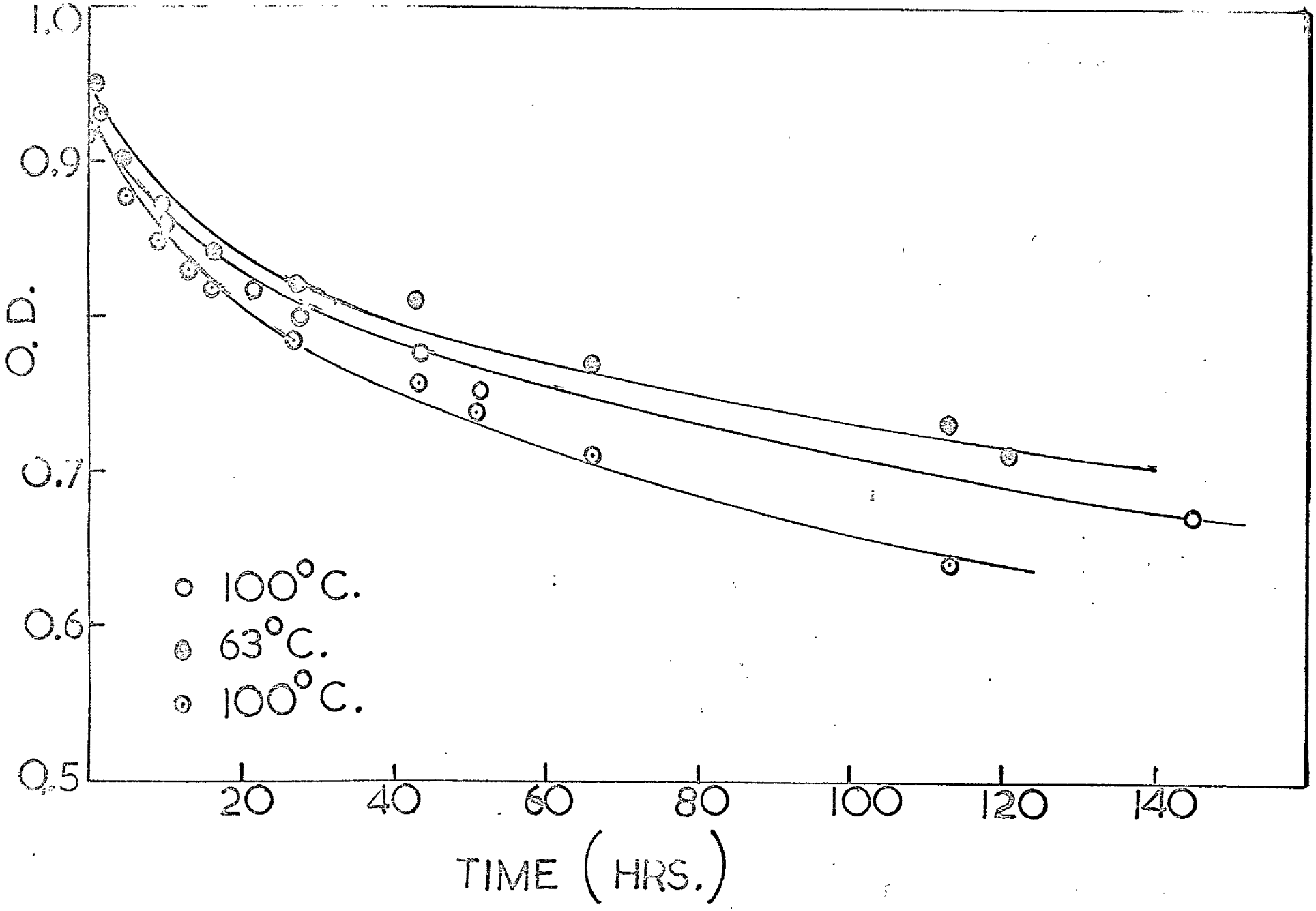
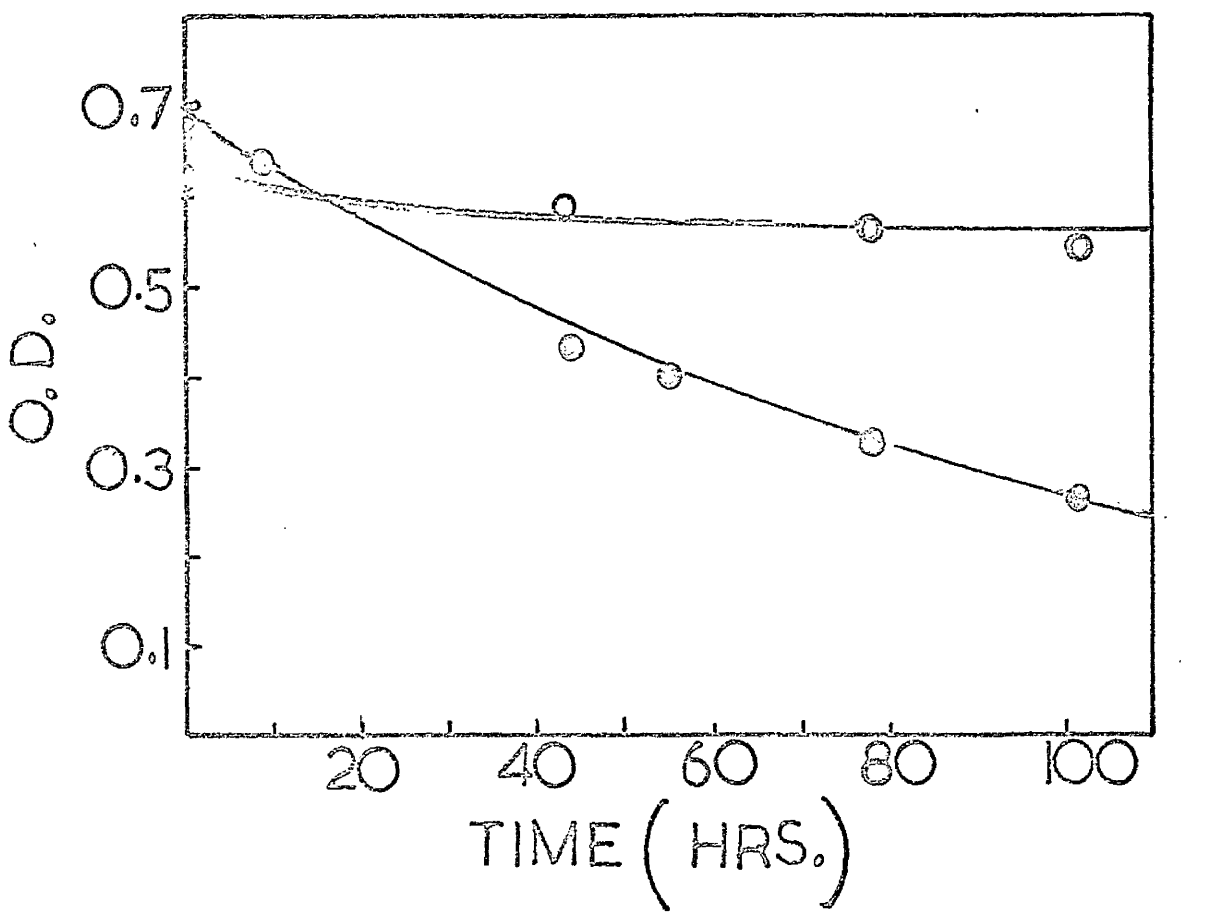


Fig.22

Legend for Fig. 23 Duranol Brilliant Yellow 6G on polyester.



○ WITH FILTER ; ⊙ WITHOUT FILTER

Fig. 23

Legend for Fig. 24 and 24(a) Disperool Fast Orange A on polyester. Fading occured at two different temperatures and humidities.

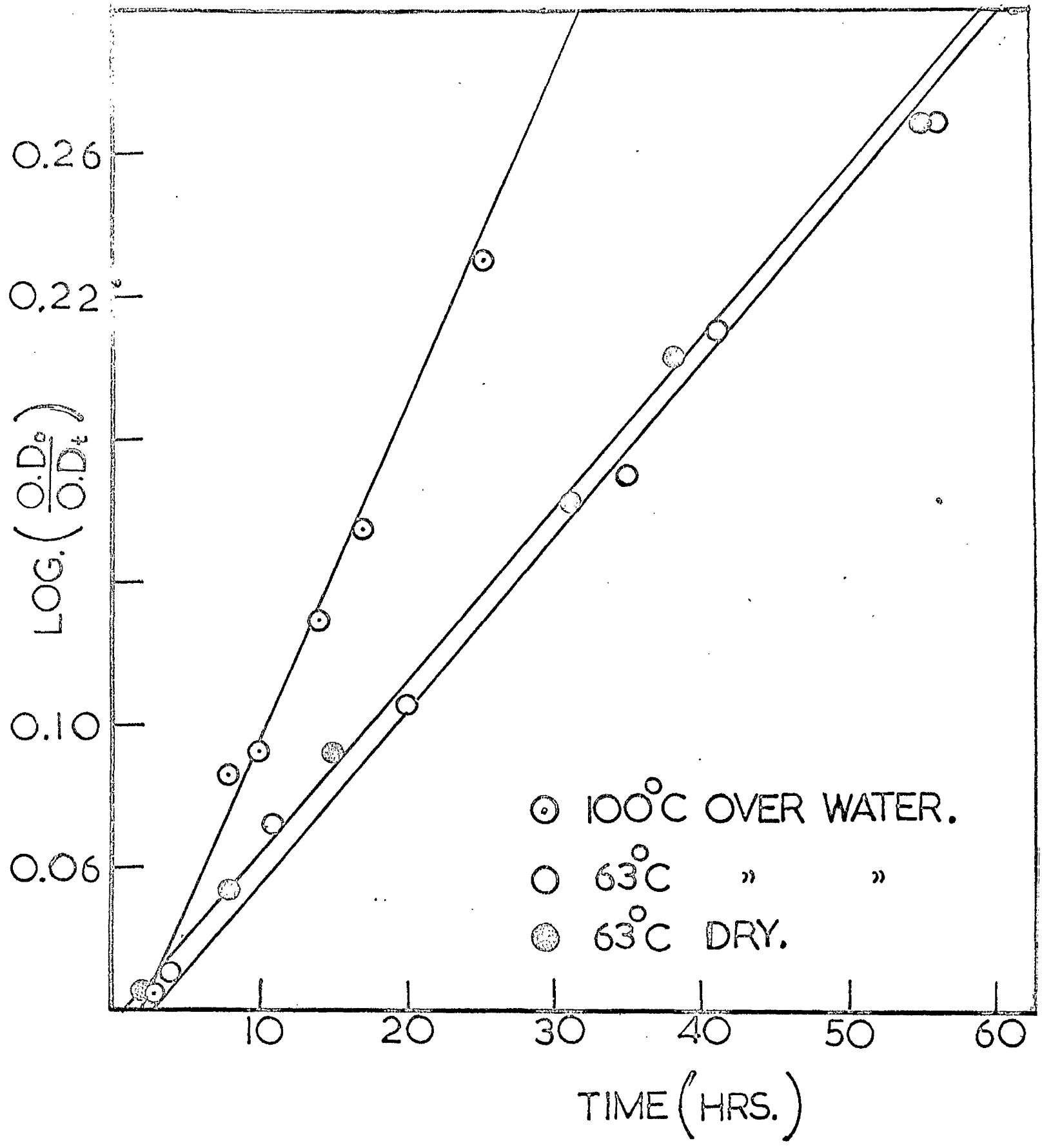

0.26
0.22
0.10
0.06
LOG. (O.D.° / O.D.t)
100°C OVER WATER.
63°C » »
63°C DRY.
10
20
30
40
50
60
TIME (HRS.)

Fig. 24

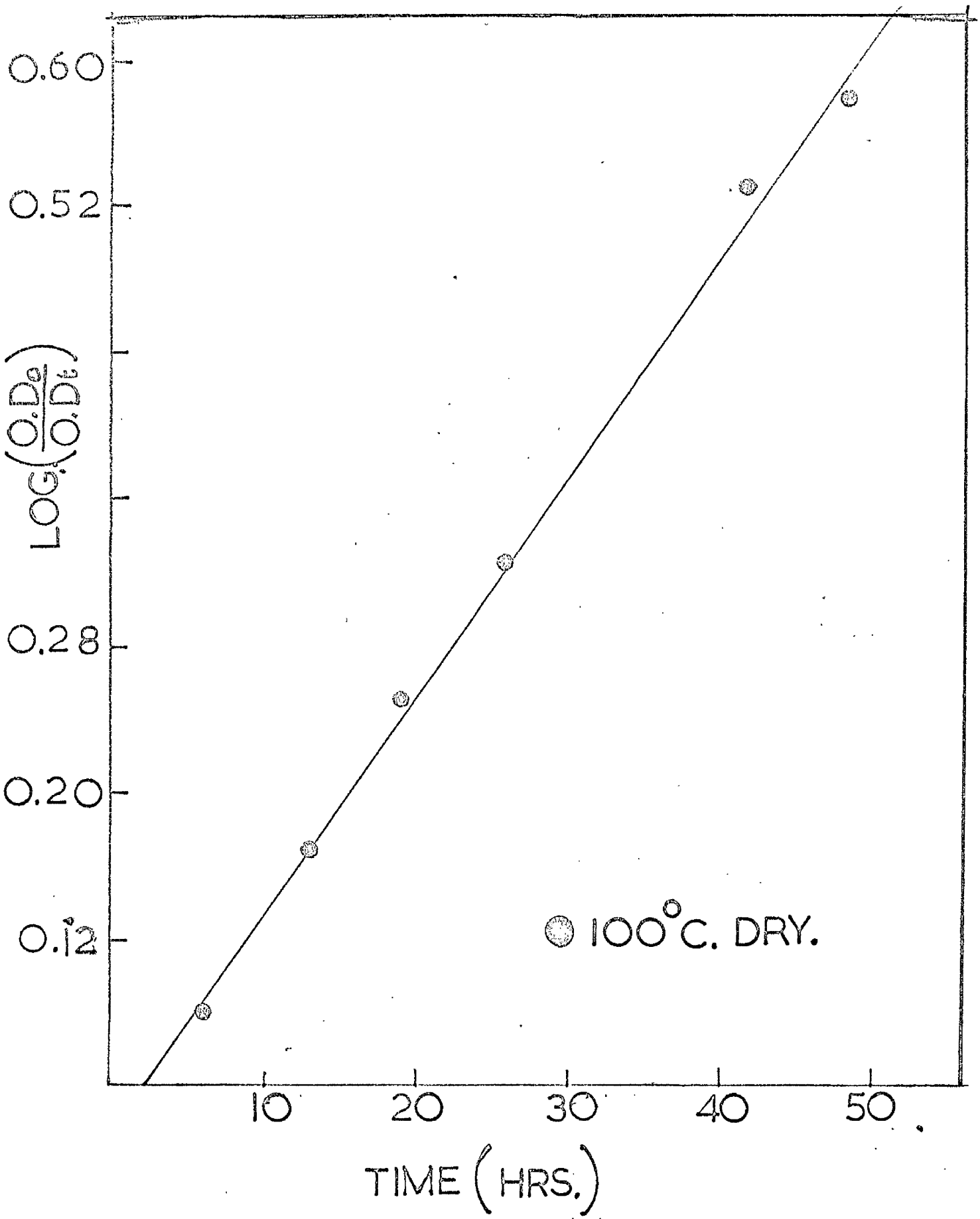


Fig. 24 (a)

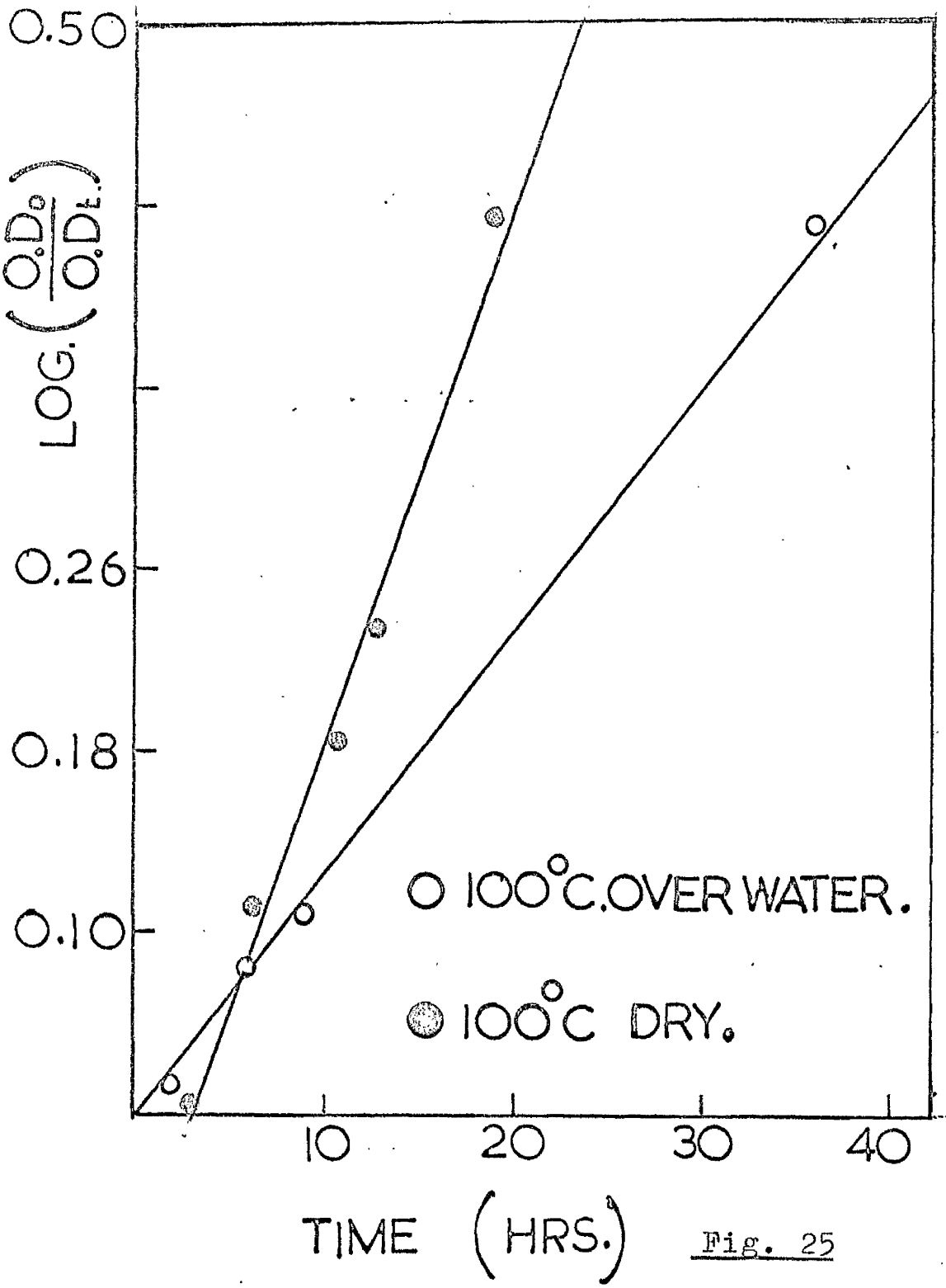


Fig. 25

Legends of Fig. 25 Duranol Violet 2R on nylon
Fading occured in two different conditions.

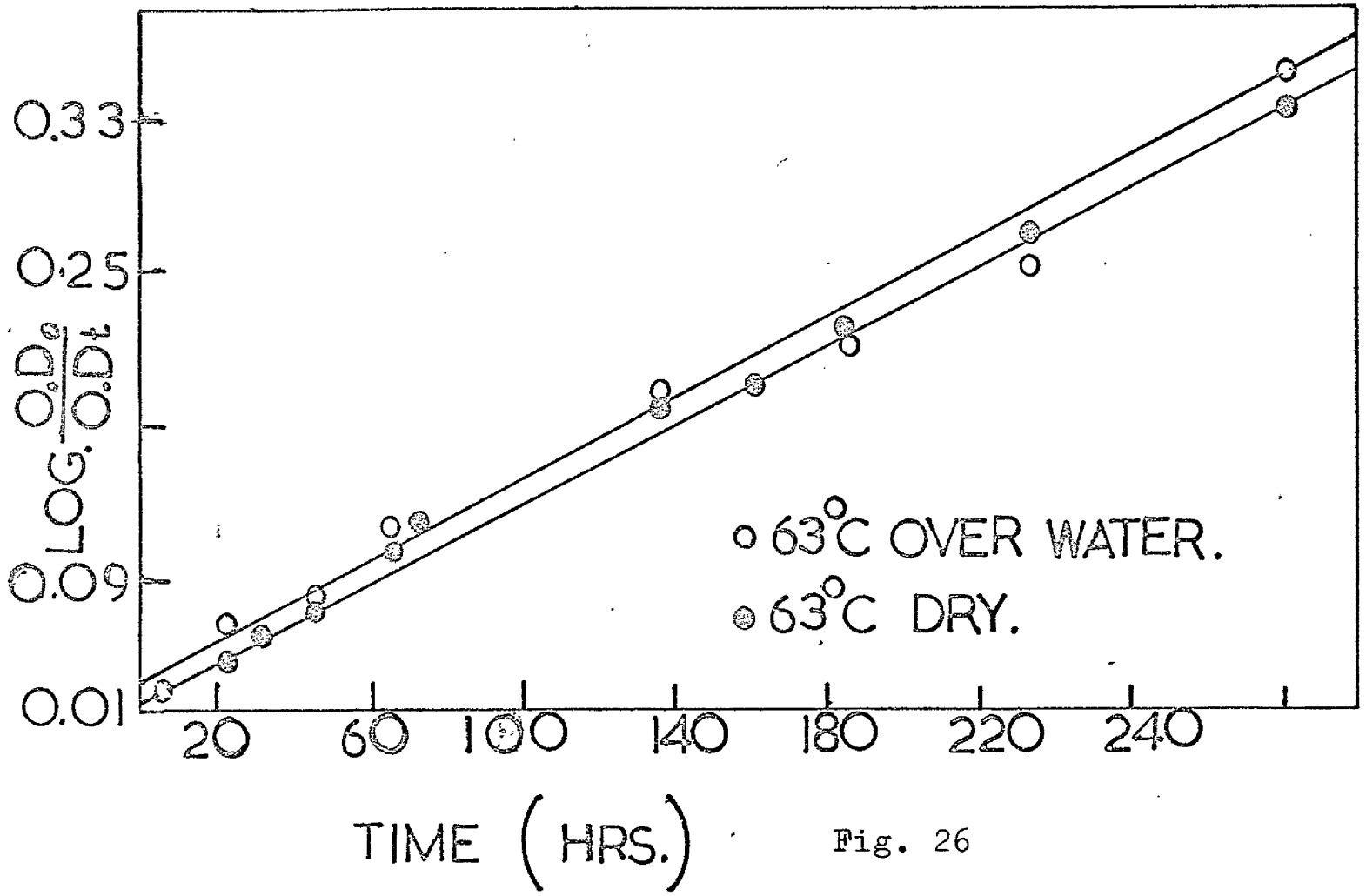


Fig. 26

Legends of Fig. 26 Duranol Violet 2R on nylon.

Legend for Fig. 27 Duranol Violet 2R on disoriented polyester.

Fading occured in two different conditions.

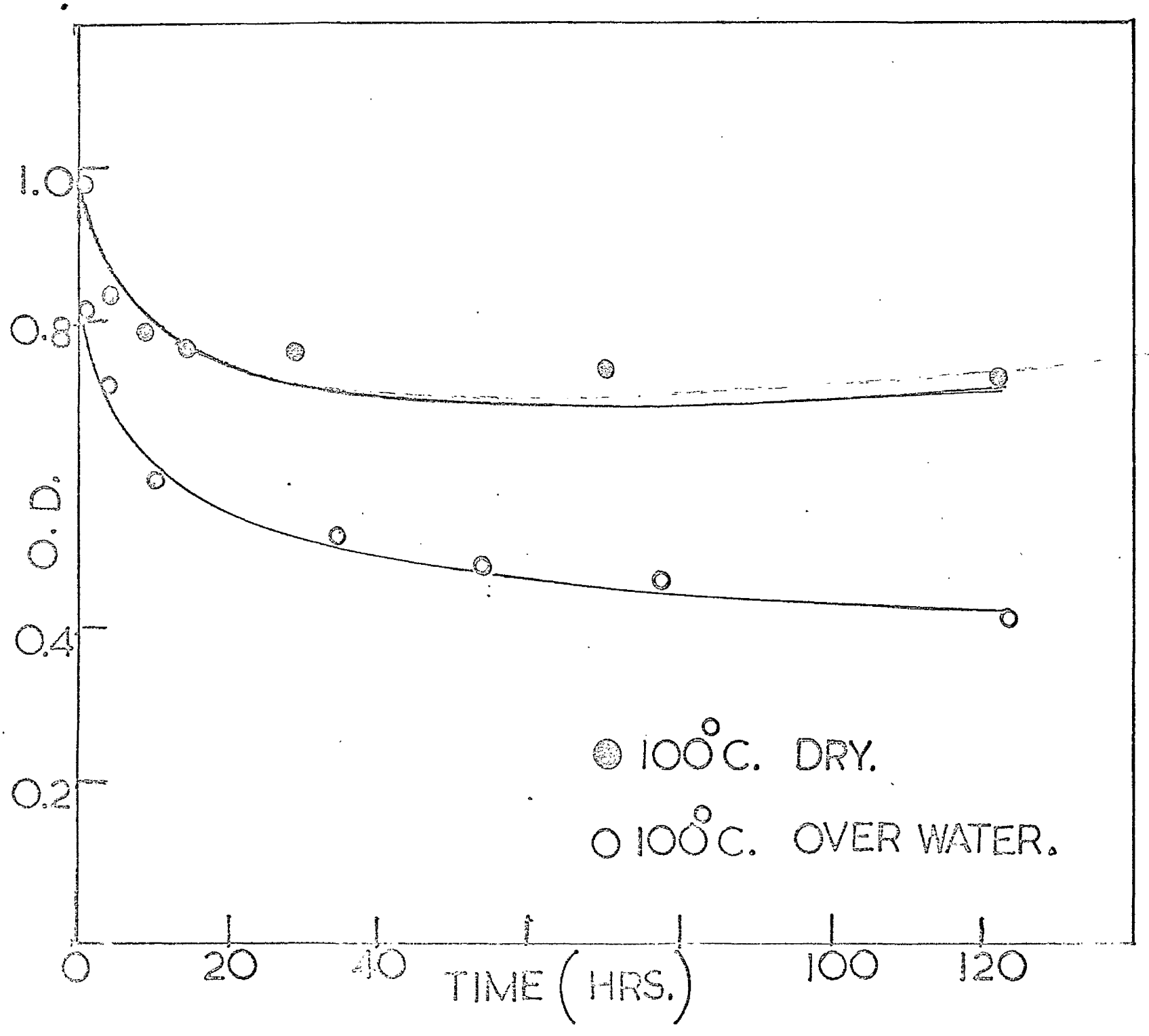


Fig. 27

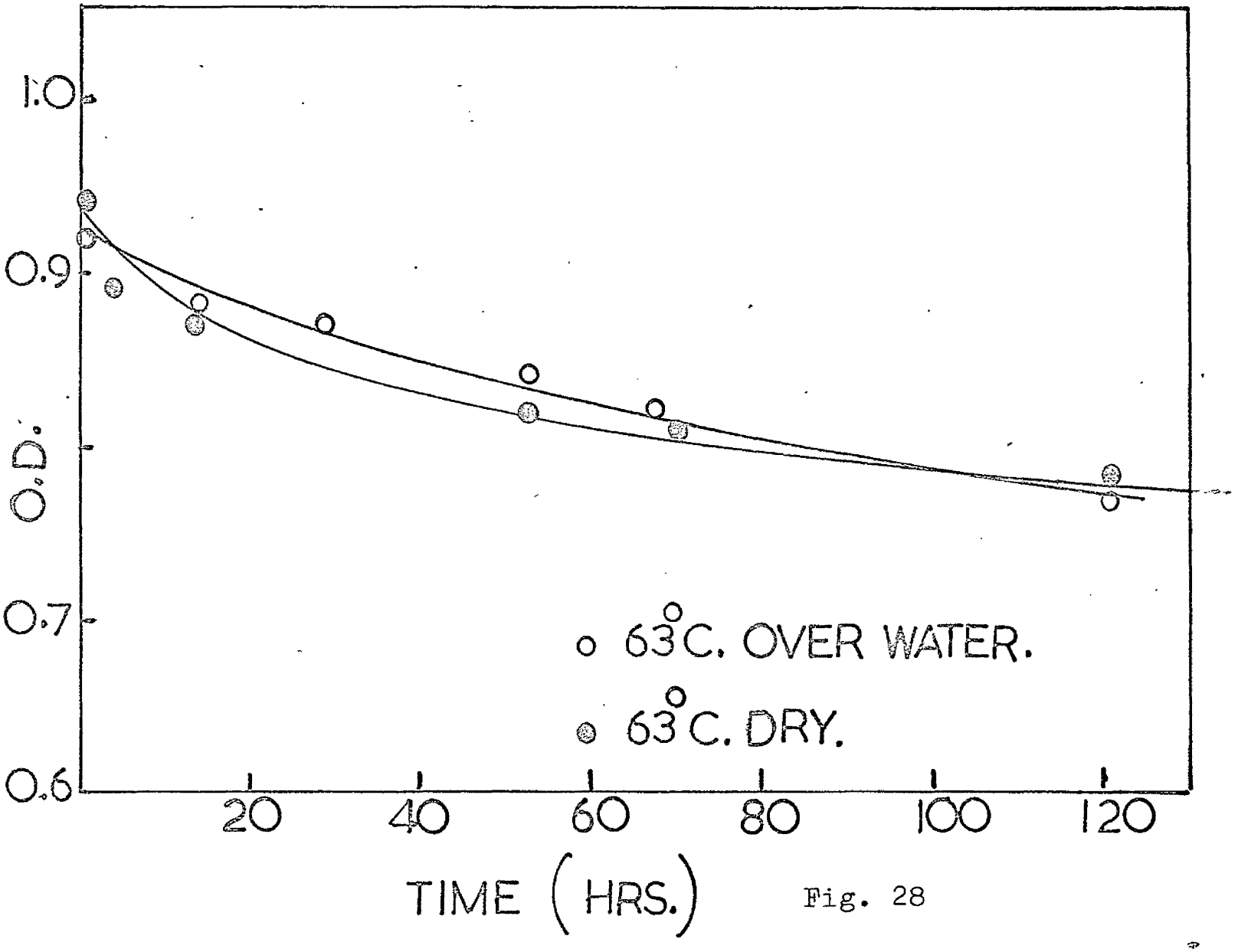


Fig. 28

Legends of Fig. 28 Duranol Violet 2R on disoriented polyester.

Legend for Fig. 29 Solway Ultra Blue B on gelatin.

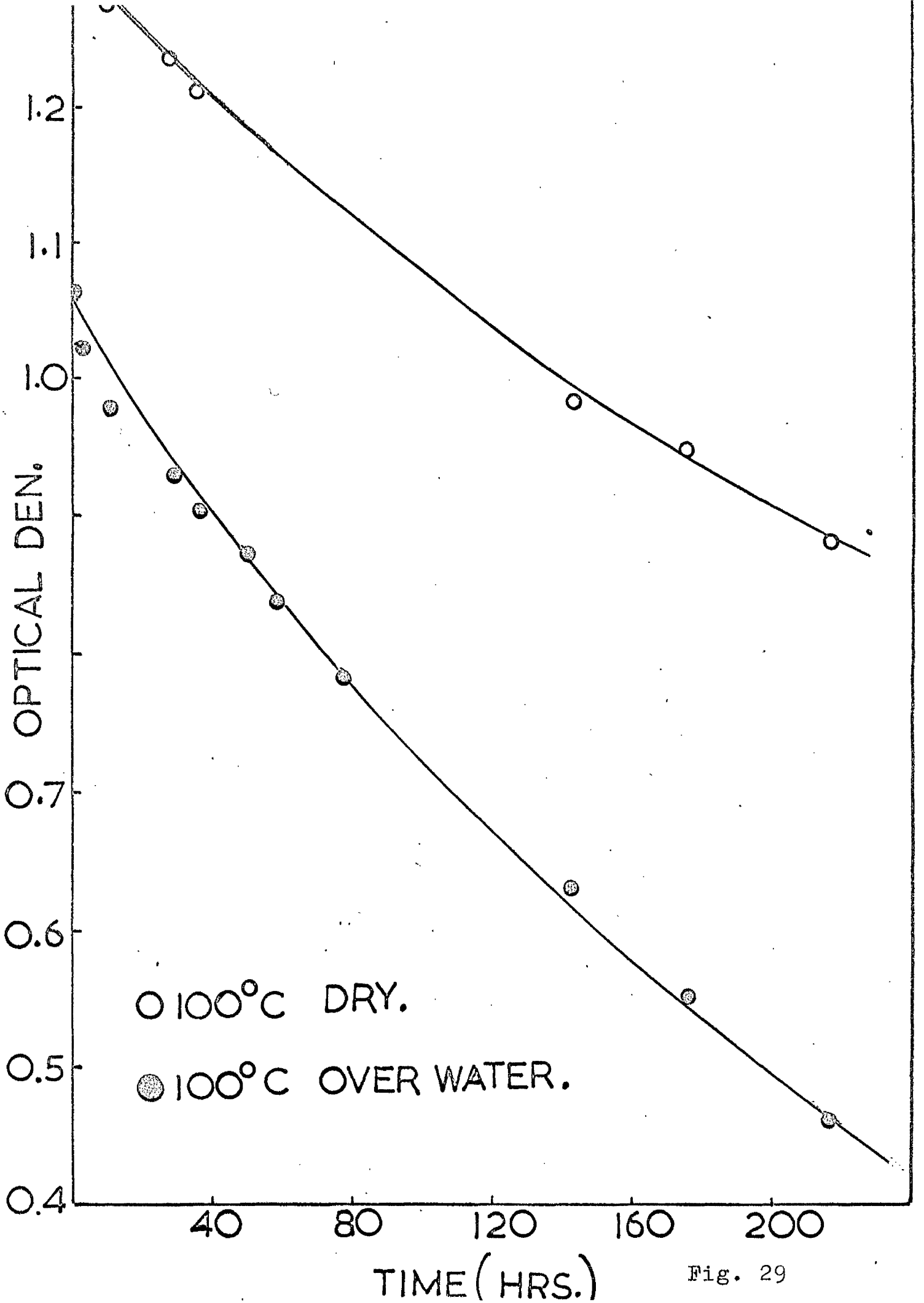

1.2
1.1
1.0
0.7
0.6
0.5
0.4
OPTICAL DEN.
100°C DRY.
100°C OVER WATER.
40
80
120
160
200
TIME (HRS.)

Fig. 29

Legend for Fig. 30 Solway Ultra-Blue B on gelatin.

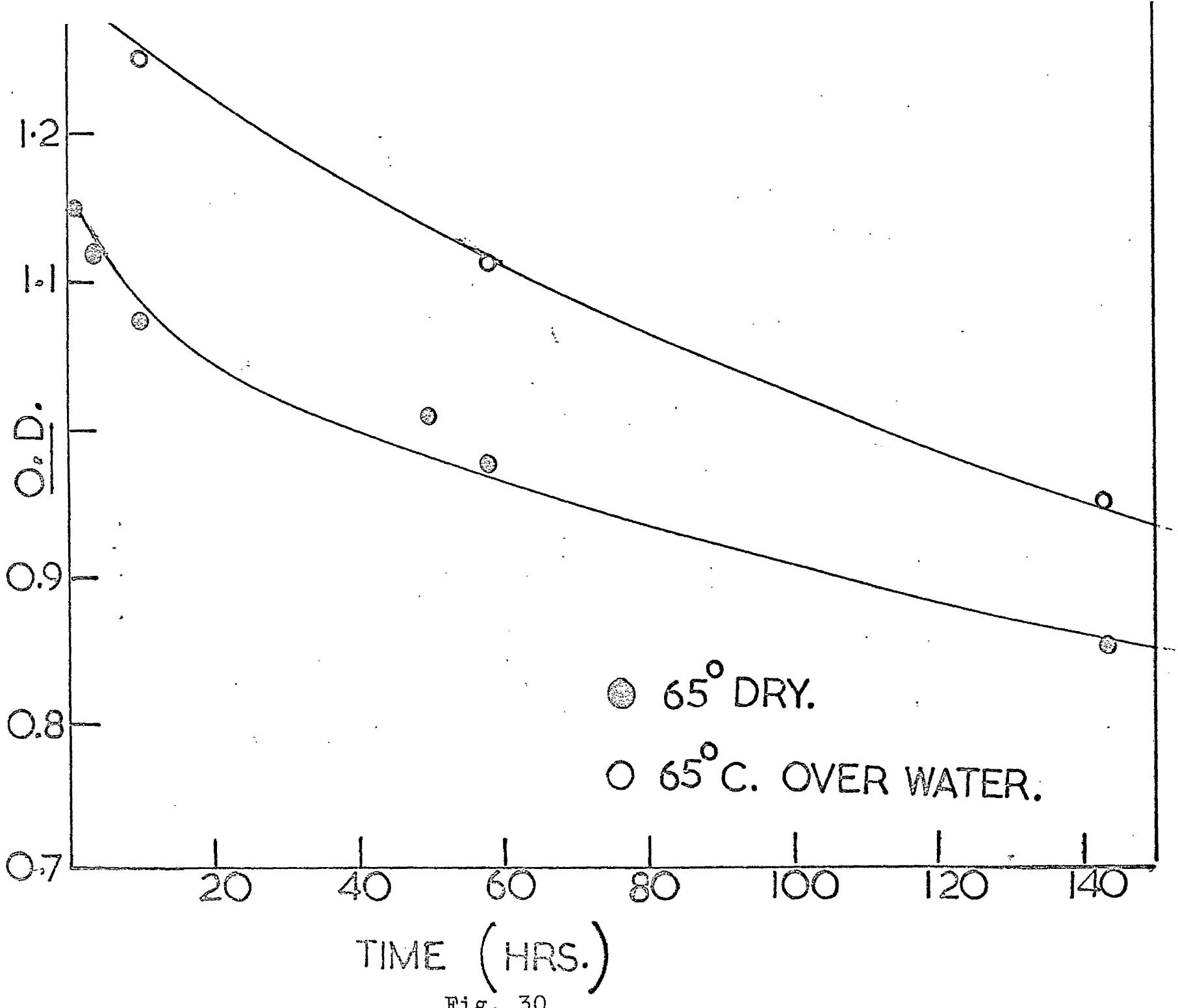

1·2
1·1
O.D.
0.9
0.8
0·7
20
40
60
80
100
120
140
TIME (HRS.)
65° DRY.
65°C. OVER WATER.

Fig. 30

Legend for Fig. 31 Dispersol Fast Yellow A on polyester.

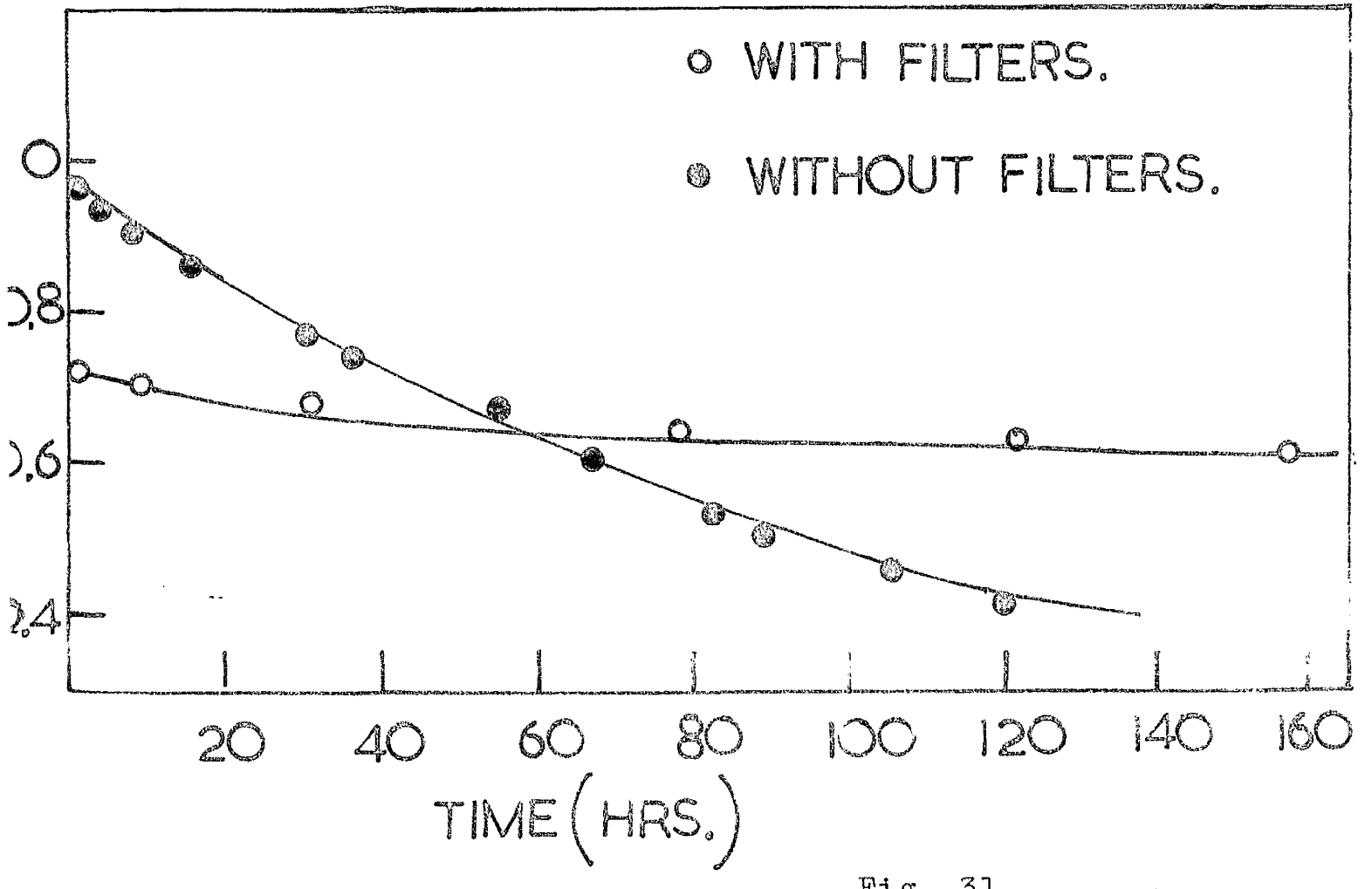

o WITH FILTERS.
• WITHOUT FILTERS.
1.0
0.8
0.6
0.4
20
40
60
80
100
120
140
160
TIME (HRS.)

Fig. 31

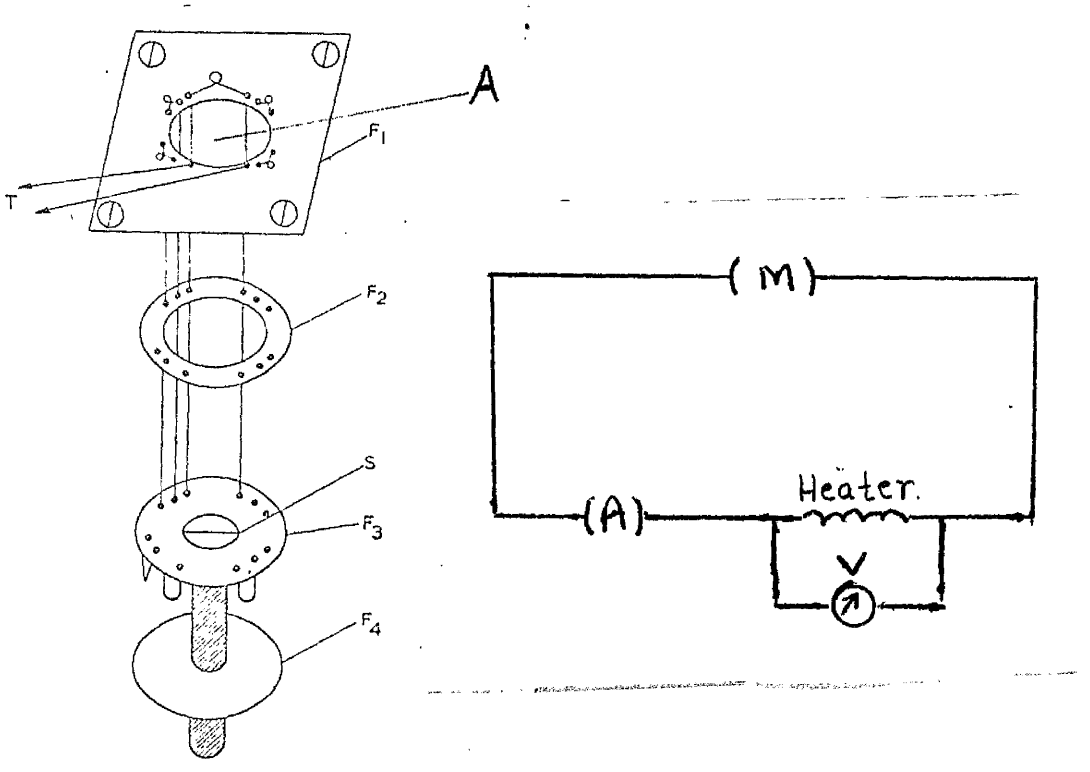


Fig. ■ Ampoule heater. For simplicity only a few heater windings are shown.

Fig. 32 Ampoule heater.

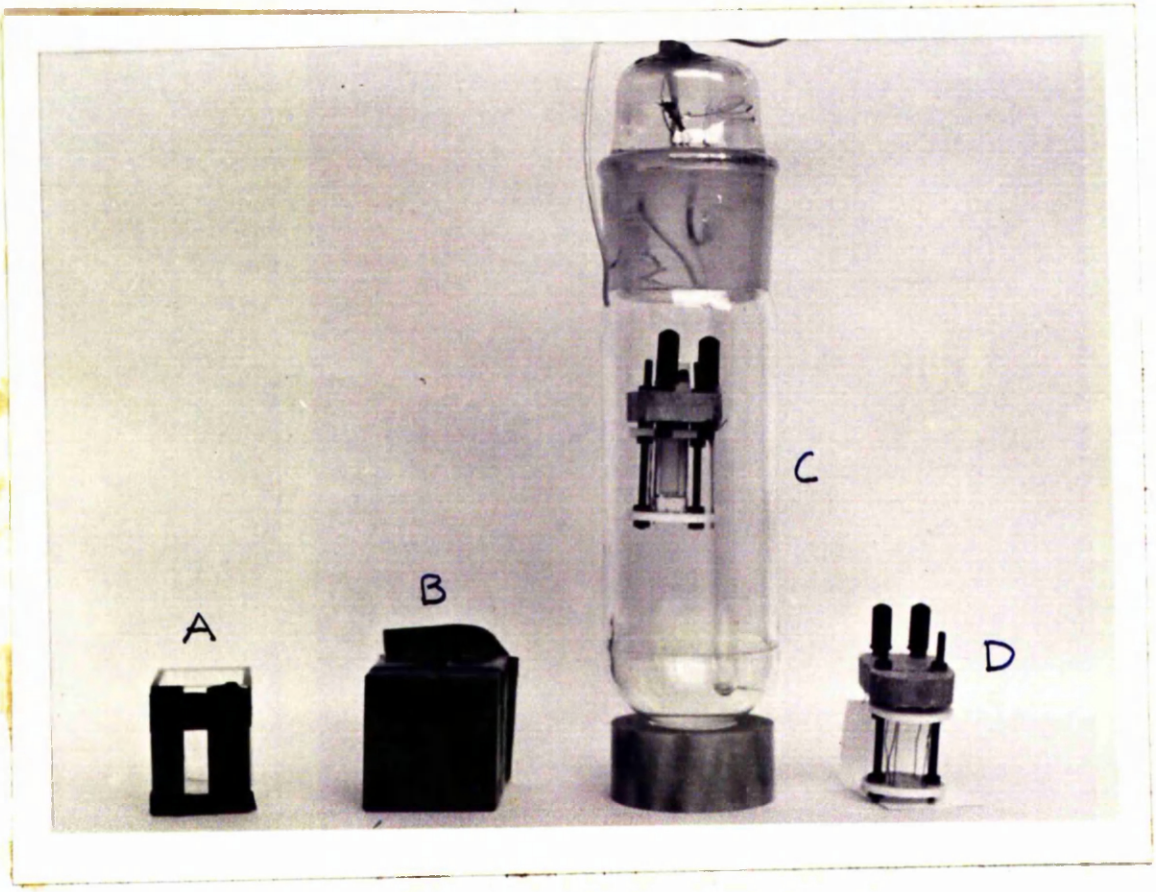


Fig. 33 Apparatus used in fading and quantum efficiency experiments.

(A) Actinometer cell

(B) Brass box

(C) "PYREX" tube used in fading experiment to obtain dry and wet conditions.

(D) Temperature control device (heater)

Legend for Fig. 34 Relation between x/y ÷ Molecular weight and light-fastness of all Direct dyes on cotton.

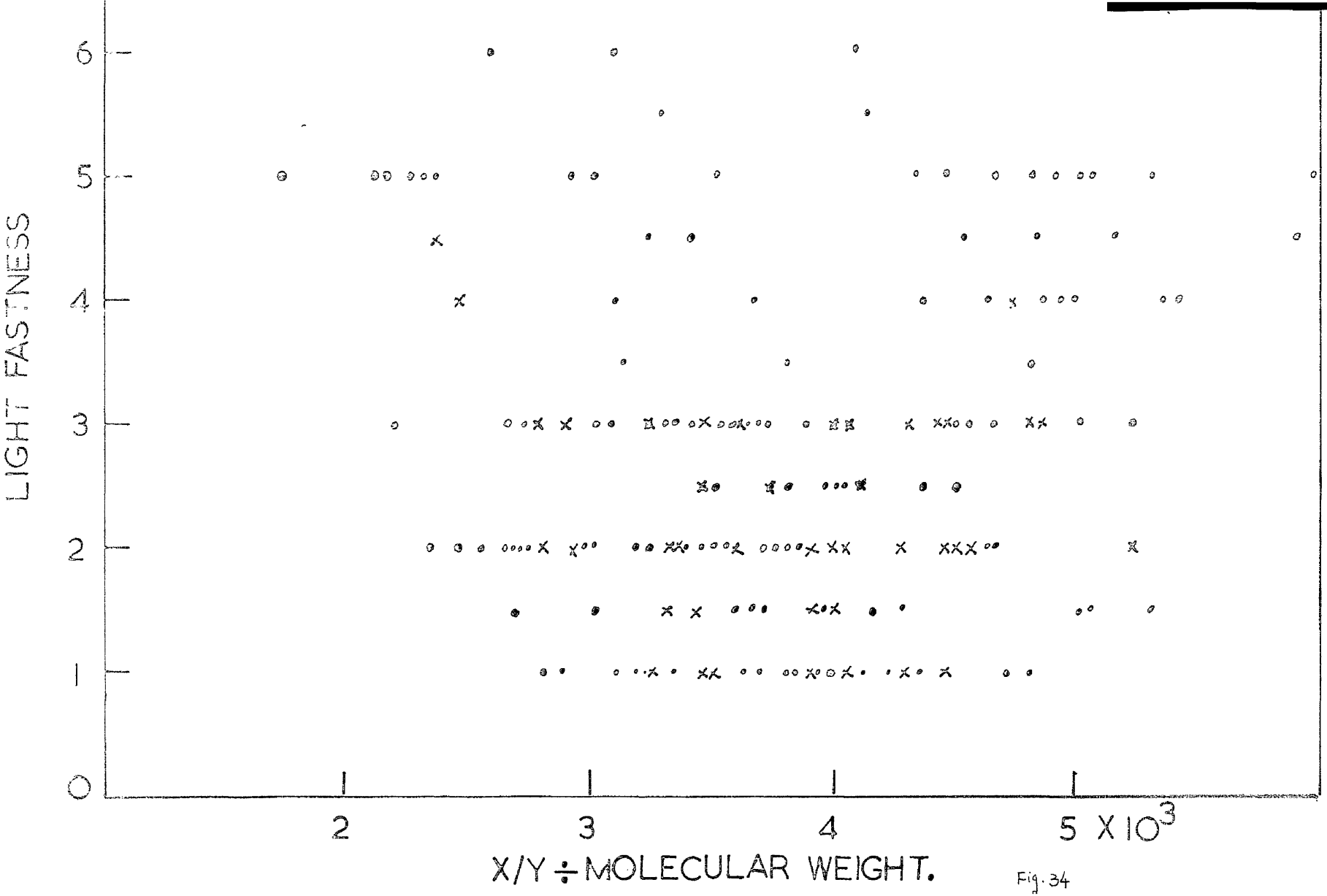


Fig. 34

Legend for Fig. 35 — Relation between x/y ÷ Anionic weight and light-fastness of all acid dyes.

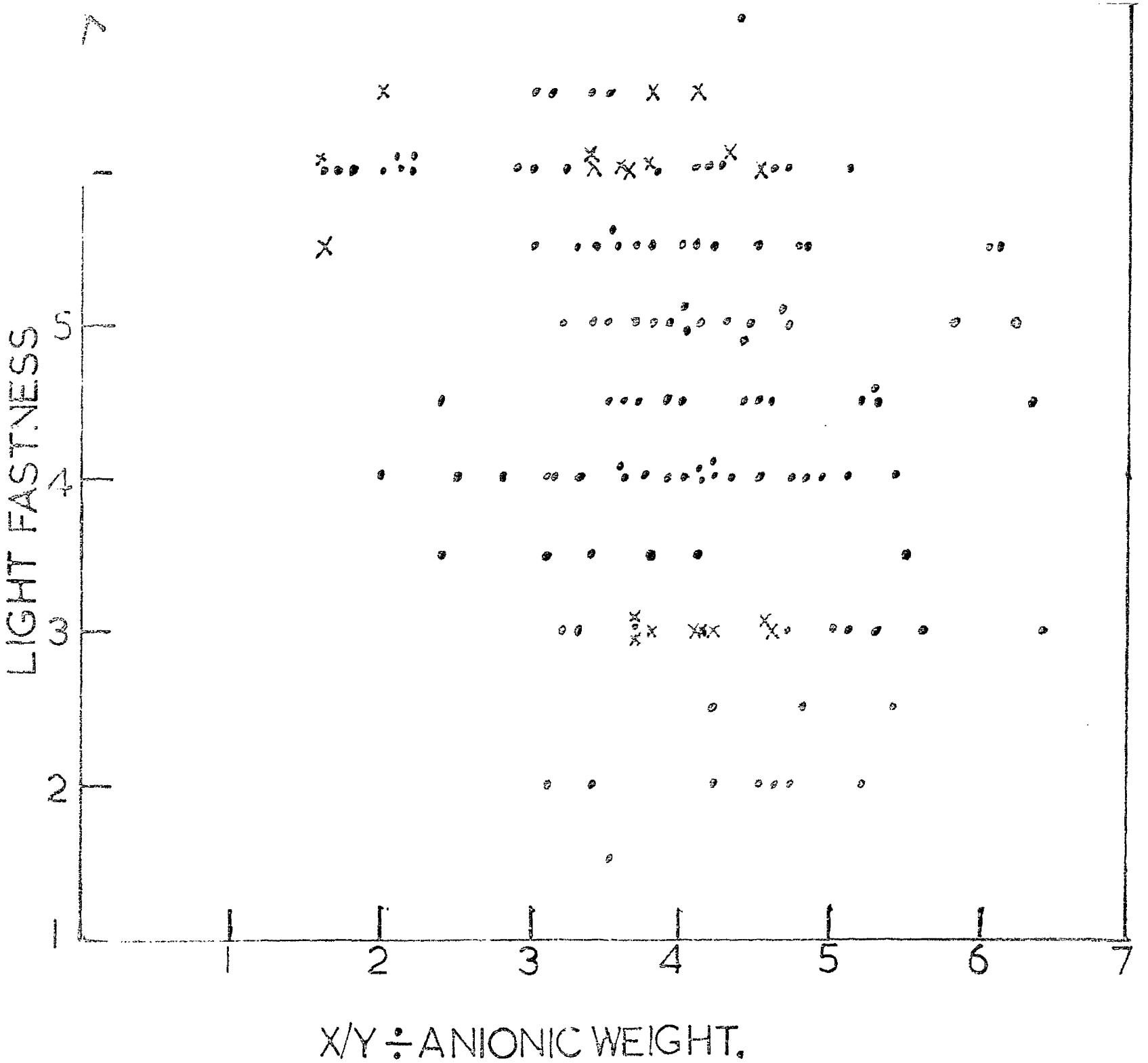


Fig. 35

Legend for Fig. 36 — Relation between x/y ÷ Molecular weight and light-fastness of anthraquinone vat dyes.

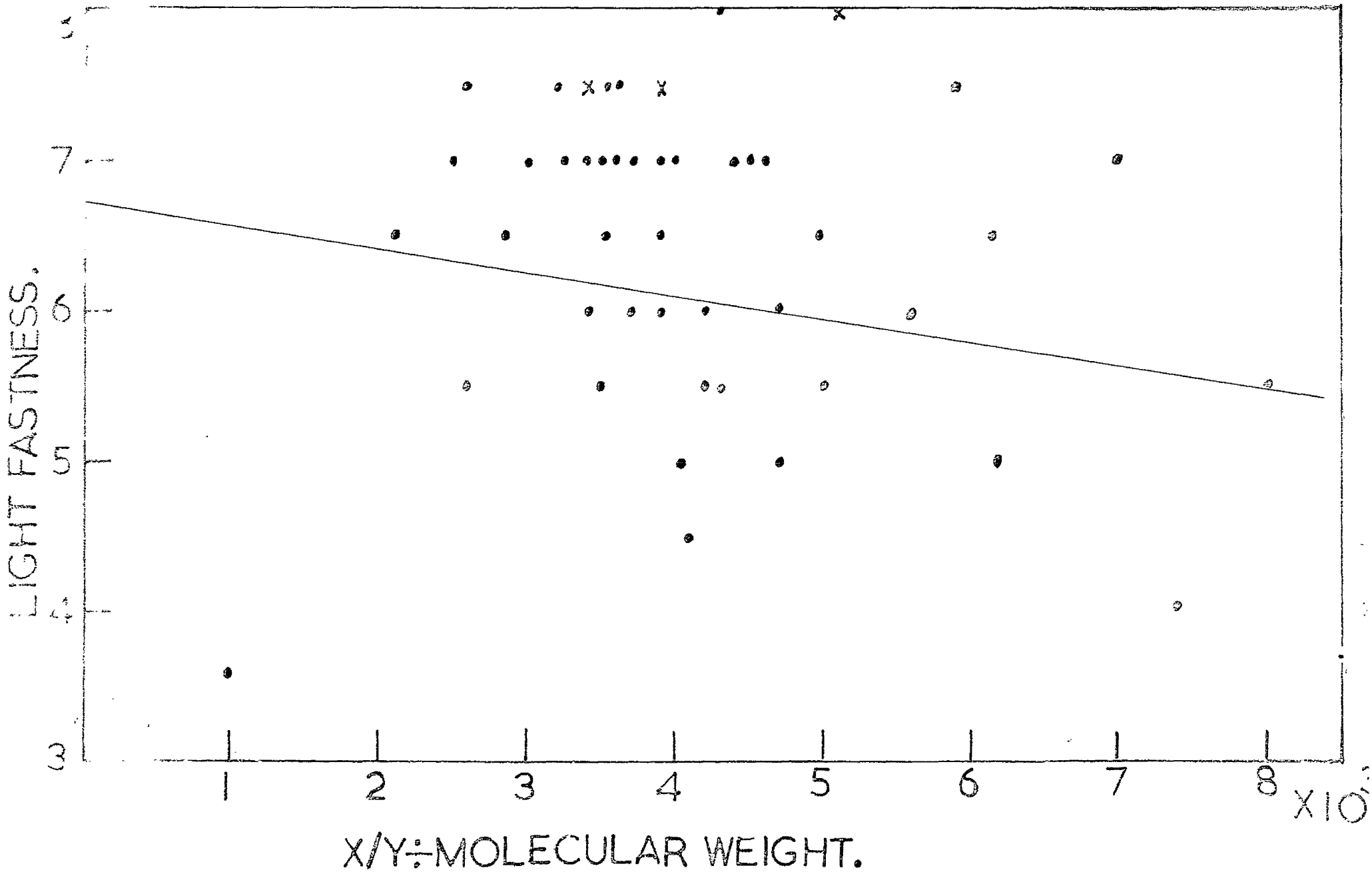


Fig.36

Legend for Fig. 37 Relation between x/y ÷ Molecular weight and light-fastness of Disperse dyes.

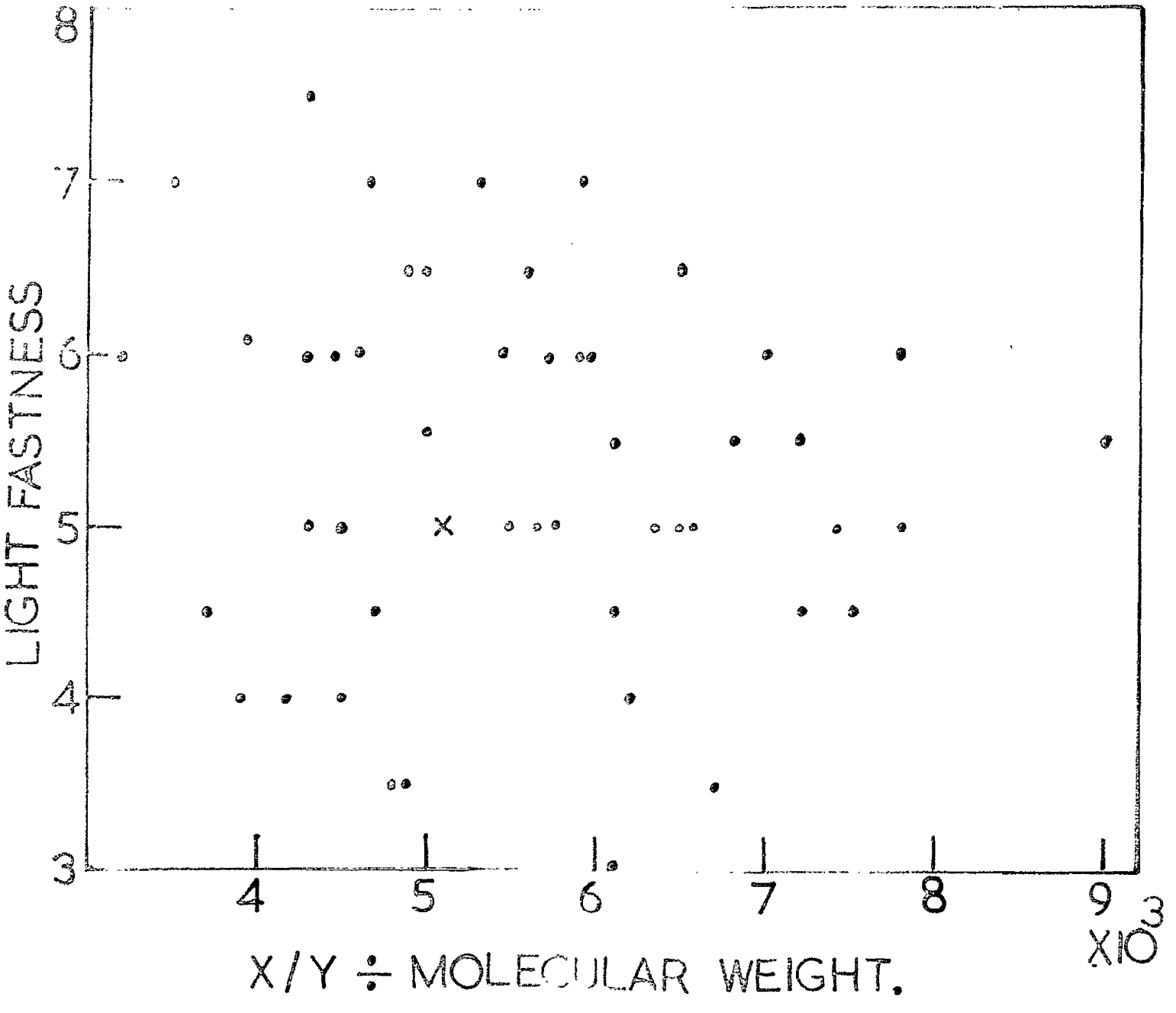


Fig.37

Table XV

Monosulfonated acid dyes

C.I. No.	x	C.I. No.	y
18695		17060	
13100		17080	1.75
50205		13455	1.45
18820		62010	1.4
18830		68500	1.55
18960		62020	1.8
11230	2.05	60730	1.75
18835		62160	2.3
18900		62055	1.6
13065		61530	1.5
18950		62125	1.9
19025		62130	1.9
18915		63000	1.3
11170		62085	1.7
13200	1.7	62145	1.9
18850		62135	1.6
13080			
11270		63315	1.35
15575	1.6	62045	1.6
15540	1.6	62105	1.7
20160	2.15	62155	2.0
17770	2.2	17055	
14710	1.65	17605	
14680		14610	1.75
15635		14805	1.9
15640	1.9	14625	1.6
17065		13000	1.9
17070	1.85	17640	
17920		17580	
68215	1.55	14675	1.7
68200	1.45		
68220	1.15		
15620	1.6		
26420	1.8		
14695	1.8		
15625	1.8		
26665	2.1		
26900	2.35		

Fig. 38 [illegible] between [illegible] atomic weight [illegible] monosulfonated acid dyes. [illegible] least squares line shows [illegible] of the relation

Table XVI ons

B. *Anthraquinone Vat Dyes*

C.I. No.	x y	C.I. No.	x y
58950	2.82	69825	1.63
59100	1.7	69815	1.9
59300	1.25	69850	1.81
59700	1.7	70600	1.75
59800	2.3	70695	2.04
59825	1.86	71135	3.06
59835	1.77	71140	3.23
59850	2.53	56050	2.05
59820	2.32		
60005	2.3		
60015	1.61		
60765	3.06		
61650	1.52		
61655	1.52		
61670	2.24		
61725	2.0		
63355	2.0		
63365	1.92		
64015	1.39		
65400	2.2		
65405	3.3		
65410	2.14		
65415	2.1		
65420	3.3		
65425	3.3		
65435	2.87		
67820	2.85		
67895	1.68		
67900	1.68		
67910	1.5		
67915	1.57		
67920	1.41		
68000	1.78		
68400	1.43		
68405	1.65		
68420	1.77		
68700	2.3		
69500	2.3		
69515	2.45		
69450	.16		
6950	2.16		
69815	1.63		

Fig. 39 Relation between light-fastness and molecular axial ratio (MAR) for anthraquinone vat dyes. The least square line accounts for 26% of the regression.

Legends for Table XVII and Fig. 40

Table XVII — Relation between percentage fading caused by Blue-to-Red Region of the spectrum

Fig. 40 — Relation between MAR of dyes with planar molecules and effectiveness of the blue-red spectral region in causing fading. The least squares line shown accounts for 52% of the total regression. Dye classes: × acid; ○ , direct; ● , disperse; △ , vat.

Table XVII Relation Between Percentage Fading Caused by Blue-to-Red Region of the Spectrum (McLaren's data [3]) and MAR*

C.I. No.			% Fading by blue-red region	MAR, x y
Acid dyes	Violet	1	3	1.8
	Black	24	12	2.0
	Blue	78	20	1.7
	Green	19	75	2.5
	Green	20	32	2.3
	Orange	10	17	1.5
	Blue	113	75	2.0
	Violet	41	5	1.8
	Blue	40	3	1.9
	Blue	27	29	1.5
	Green	27	17	1.4
Direct dyes	Green	6	68	2.9
	Violet	22	83	2.8
	Blue	1	87	3.2
	Blue	20	83	3.0
	Black	38	68	2.8
Vat dyes	Violet	17	16	1.9
	Violet	9	46	2.3
	Green	9	39	2.5
	Green	1	20	1.9
	Violet	13	1	2.3
	Violet	2	55	2.1
	Brown	5	71	2.0
	Violet	14	1	1.7
	Red	1	53	2.4
	Blue	5	6	2.1
Disperse dyes	Blue	7	8	1.2
	Violet	8	26	1.3
	Blue	3	16	1.3
	Blue	24	22	1.4
	Violet	4	18	1.3

* From McLaren's list all the dyes with planar molecules have been selected.

Fig. 40 Relation between MAR of dyes with [illegible] molecules and effectiveness [3] of the blue-red spectral region in fading [illegible]. The [illegible] squares line shown accounts for 52% of the total regression. Dye classes: [illegible] direct; ● [illegible] Vat.

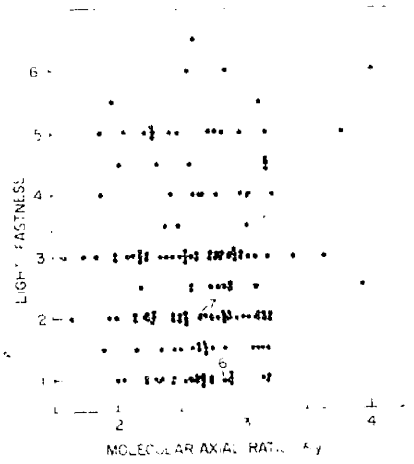


Fig. 41 Relation between LF and MAR for all direct dyes on cotton.

Fig. 41 Relation between light-fastness and MAR for all direct dyes on cotton.

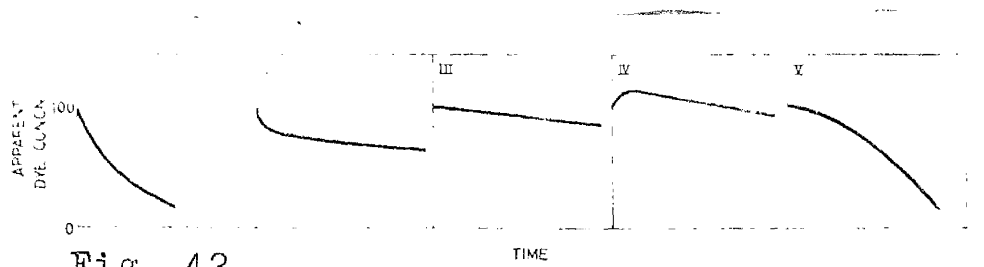


Fig. 42 *Diagram of types of fading-rate curves of colorants*

I. First- or second-order fading. Dye probably in molecular dispersion. Rarely occurs.

II. Initial rapid fading followed by a slow fading at a constant rate (zero order). Dye probably partly in molecular dispersion and partly particulate. Occurs most often.

III. Constant rate of fading. Dye probably entirely particulate. Occurs often with [illegible] dyes.

IV. Negative initial fading caused by disintegration of dye particles in the light of illumination. Occurs with [illegible] dyes.

V. Fading which accelerates with time. Caused by continued breakdown of dye particles. Obtained with some insoluble azo dyes in cellulose.

Fig. 42 Diagram of types of fading-rate curves of colorants.